A. T. Shulgin

Chem notes: Book #8

many found during post-Thursday clean-up.

Thursday, October 27, 1994 - the BIG day!

harmala alkaloids	5-substituted
H_2 → me Quat 161	5-MeO-DIPT 108, 109, 121, 167, 265
H_2 → Ho 133	5-MeO DALT 264

Tryptamines: Ms's or NMR's ↓

DSBT 58
EIPT 56
α,N,O-TMS 5
NMT 22
MIPT 32, 125
MSBT 34
MPT 36 (DPT) 838485
DALT 38 (NALT)
NET 54, 64 (di)
NSBT 58 (DSBT) (T)
NIPT 60
NPT 62 (DPT)(T)
DMT 66 (T, NMT,)(carboline)
70-71, 1-methyl, carboline

mor
pip
pyr 102, 104
5-meo 132 mp
T 132 mp.

MIPT quat 125

Cacti: Red-blossomed T. grandiflorus 137
Yellow-blossomed T. grandiflorus 147
Red T. grandiflorus #2 148

Peganum harmala: 48
Tetrahydroharmine: 44

5-MeO-pyr-T 120

index isoquins!

6,7(OMe)$_2$ [138 amide
139, 141
[140 → dihydro - Tny tetrahydro
142 spectra
144 - chem
N-Me [143 spectra 162

6,7 MDO amide 145A spec 150

6,7 MDO MDPEA 186 → 190
formamide 191

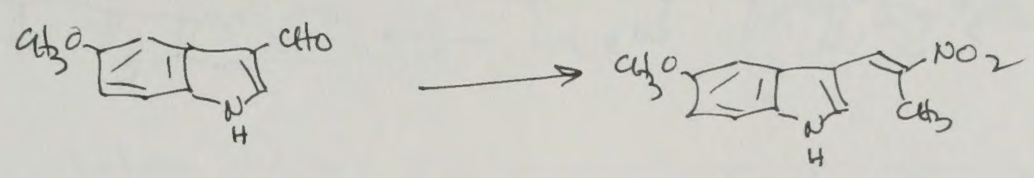
DMHH-4 NH_2 → formate 170
formate → DHIQ 171, 172
→ THIQ 174, 207

5-H / 5-MeO	H	M	E	P	AL	IP	B	IB	SB	TB
H	T 5 MeoT	NMT 22	NET 52, 54	NPT 62		NIPT 60				
M	5-MeoNMT	DMT 5-MeoDMT	MET			MIPT 32				
E	5-Meo-NET 101	5-MeoMET	DET *** 65 64, 86 96 97 5Meo DET 94, 95			EIPT				
P				** DPT 62, 83 84 85 5-MeoDPT 105 *		PIPT 106				
A										
IP						DIPT *** 87, 89, 99, 100 5-Meo-DIPT 87 109 88, 90, 92, 98 228				
B										
IB										
SB										
TB										

	pyr H4	pyr H8 [illegible]	pip.	morph	α	α,N	α,O	α,N,O
5-H		102, 103, 104 coco 112	110	coco 113				
5-MeO		coco 115 [illegible] * 119 117 120	coco 114 *	coco 116				

* chem into T
** commentary
*** T done.
** TO GO DPT
5-MeO-DPT

(3)



2.0 g indole carboxaldehyde
25 g $EtNO_2$ Δ → sol.
0.5 g NH_4OAc SB Sol ~ 2 min 1½ hrs done by TLC stirq
↓
9 g wet orange solids

Rextal f. 20 mL boiling IPA, ∇, filter, wash
air dry
↳ 1.56 g ~~54%~~ 59% mp 179-80°

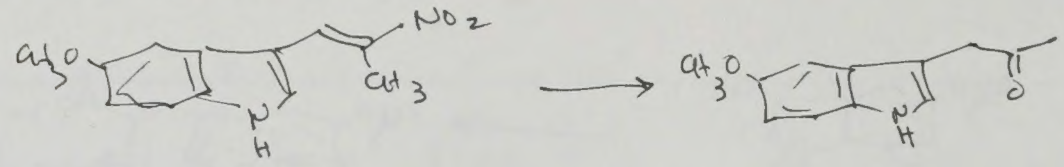
ML'S 0.81 g
xtal f. 10 mL EtOH Δ ∇
→ dull gold xtals 0.57 g mp 178.179° Σ 2.13 g 78% theo.
lit 182-184° mp. reference (3)
0.57 g

repeat ———————

1.21 g ArCHO
15 g $EtNO_2$
0.3 g NH_4OAc - on SB 16:20 [:20] v. dark already.
off (1:15)

↳ 1.58 g rusty red xtals.
rextal ~~ex~~ 25 mL denatured EtOH Δ to Sol. ∇ ON
filter - wash c̄ small amt IPA -
↙ solids ML → keep
air dry. 1.24 g old gold xtals

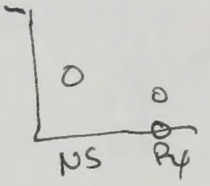
(4)



{8 ml HOAc
{2 ml H_2O } Δ on S.B. add

1.7 g electrolytic iron dust, when hot, add
0.5 g π,O - NS a glob at a time, over 2 minutes

TLC
CH_2Cl_2
hexane



10 min all NS gone - new spots at origin
& in between

30 min off (had to wait for TLC)

Into 100 ml H_2O and CH_2Cl_2 - 2 phases and scrudey inbetween - filter through paper - separate, 2×50 ml CH_2Cl_2 more - wash
$\bar{c}$ sat K_2CO_3 - flash → 0.28 g film.

KR at 0.1 mm. 130°
160
180° (vac to 0.08)
215-230° over → 0.24 g oil - off white

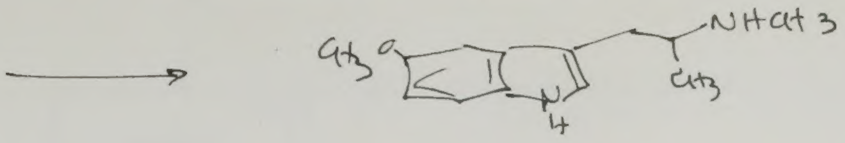
IR c=O at 1710 cm^{-1} mass spec OK.
stand a couple of months → deep brown color.

Repeat.

20 ml HOAc
5 ml H_2O } Δ SB ~ 60°. add
4.55 g Fe electrolytic - up to ~ 70° - bubbling. add
1.24 g nitrostyrene - over 2 minutes - color discharges
5 minutes OFF. - into 250 H_2O, 50 ml CH_2Cl_2 NOW
Filter through paper - wash $\bar{c}$ CH_2Cl_2. filtrate - separate - xtract aq.
$\bar{c}$ 2×50 CH_2Cl_2 - combine, flash → 1.17 g amber oil - slight
acetic acid smell

Stand 3 days in cold lab → xtals! mp - not yet by 95° - polymer?
8:4

TLC (CH_2Cl_2 2: hexane)
OK however.



α, N, O - TMS

0.22g Ketone (4) in
2.5mL IPA
add ⟶ prepare

0.3g Al strips
0.3g $HgCl_2$ soln (20g/mL)
20 min incubate.

+ 0.4 ml 40% aq. NH_2CH_3
+ 0.3 ml 25% NaOH
stand a week.

⟶ try again, with $NaCNH_3$ on the solid material 8:4

To 4.3g $NH_2CH_3 \cdot HCl$ in an E-flask - stirrer - add
20 mL MeOH, add

11 page 728 PIHKAL
1.17g Ketone 8:4 - grind in methanol - nearly all in OK. add
0.5g $NaCNBH_3$ pH green - to ~~o~~ yellow with (about) 1:1 HCl, MeOH conc.

6:00PM - 7 drops.
6:15PM 5 more
2PM next day 26 drops
2PM next day 3 drops.
2PM next day 2 drops. now then leave

into dilute H_2SO_4 - wash ē CH_2Cl_2
let evaporate.
5:00 — 40 ⟶ 8:05
disp. ...

Evaporate to 0.76g.
distill - 0.15mm
then 0.05mm.
to 180° - then over. - clear white oil
0.65 g white oil.

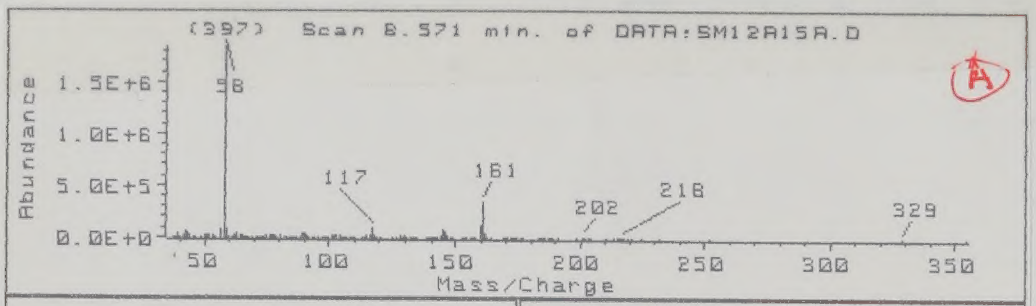
.76g.
120°
.15mm.
180 cloudy 0.5mm
0.65.

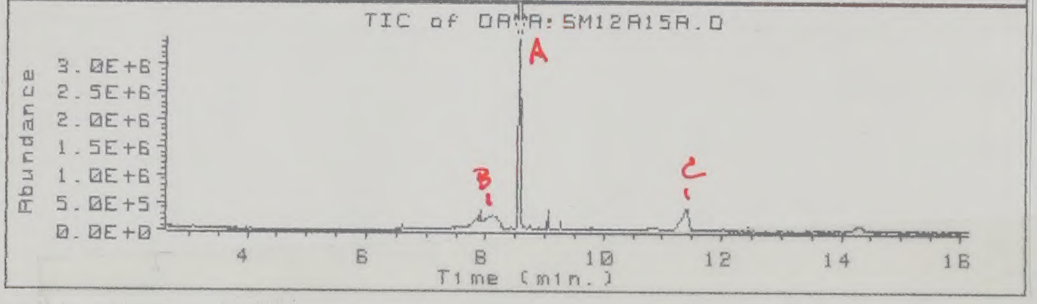
rinse out (ether, MeOH, ether)
↳ 0.58g pale yellow soln
let evaporate
(5B)

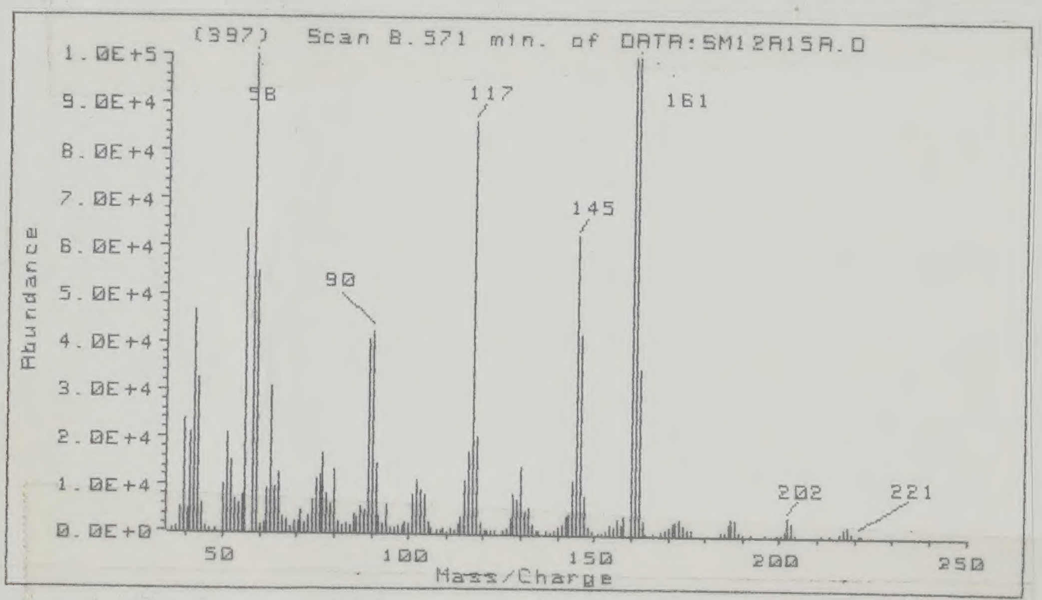
play ē IPA, CO_2 no xtals
play ē fumaric acid, IPA ether
no xtals
let stand.
(5C)

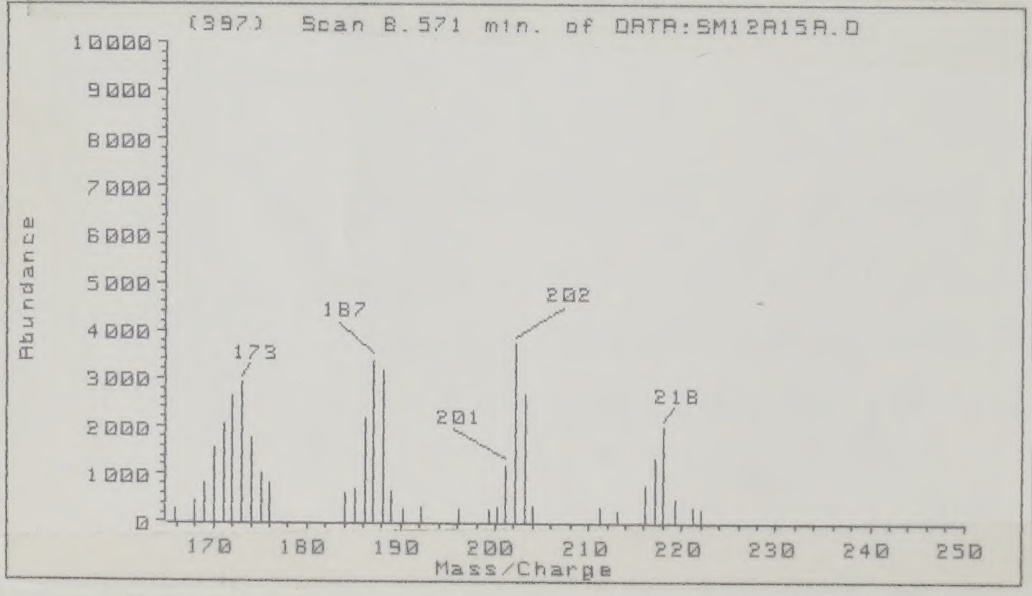
transfer to storage vial -
0.41g (5D)

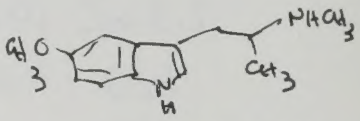
6



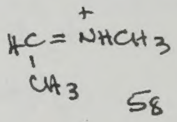




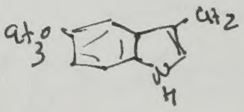




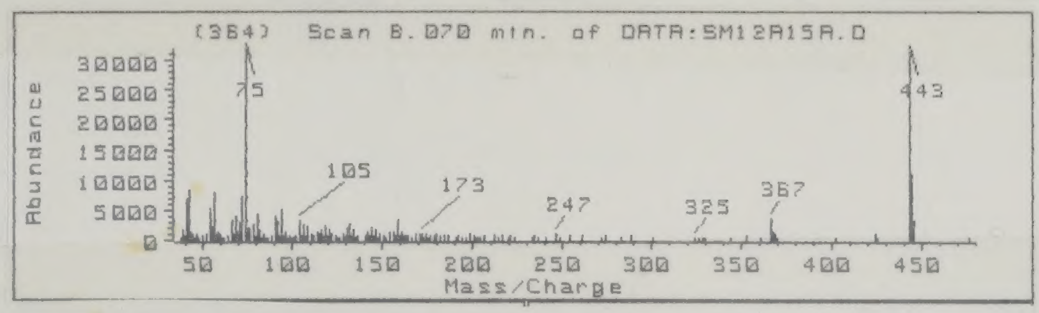
MW 218

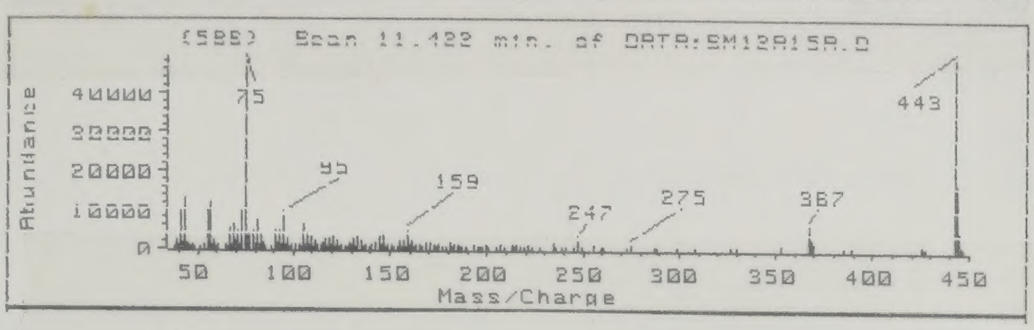


58

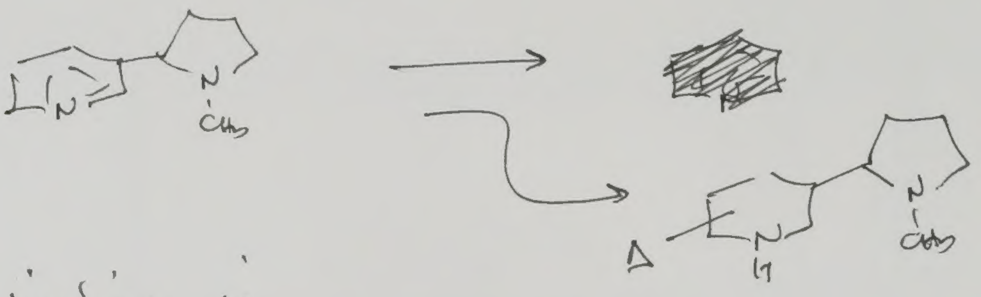


160





SIM of 203 → no Ketone.



20.5 g nicotine in
1.2 L H_2O - add
400 ml conc HCl - very good stirring - ~~[illegible]~~
200 g Zn powder
as a single addition -

2.9 g

Properties of the alkylones:

Methylone: (·HCl)
IR: (C=O) 1680 cm⁻¹ fingerprint. 720, 748, 771, 932, 1043, 1096, 1127
mp. clunky 220 (amber) shr. 230 mp 231 - 235 c̄ dec. bubbles
GCMS: cracks ~ 60/40 149/58 → 207
149/56 → 205 dehydro
See page 10, 11 MW 243

Sample 6.0 g
Nova Screen C

Diethylone: (·HCl)
IR: (C=O) 1678 cm⁻¹ fingerprint: 754, 866, 935, 981, 1041, 1086, 1110
mp: 150 amber 200 darker 204 - 205 °C quite sharp dark
GCMS: cracks ~ 70/30 149/100 → 249
149/98 → 247 dehydro
See pages 12, 13 MW 330

Sample 15.88
Nova Screen D

t-BUTYLONE
IR: (C=O) 1681 cm⁻¹ fingerprint: 888, 941, 1046, 1111
mp: 200° tan shr. 240° mp c̄ dec 247°
GCMS: cracks ~ 90/10 149/100 → 249
149/98 → 247 MW 285
See pages 14, 15

Sample VII-107
Nova Screen A

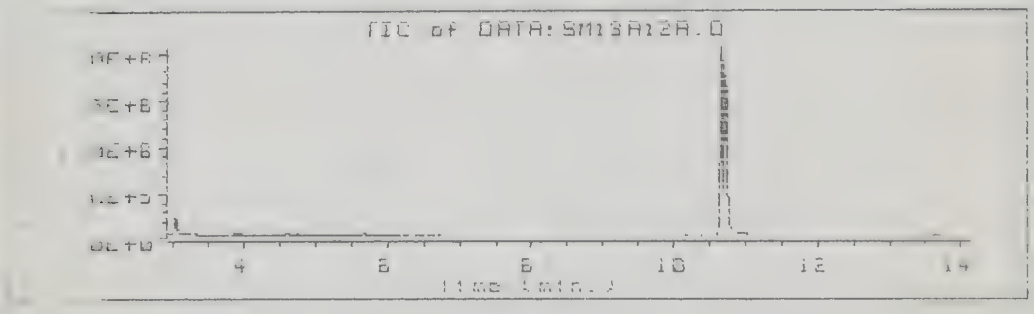
ARIADNE (racemic)

Sample I-113
Nova Screen B

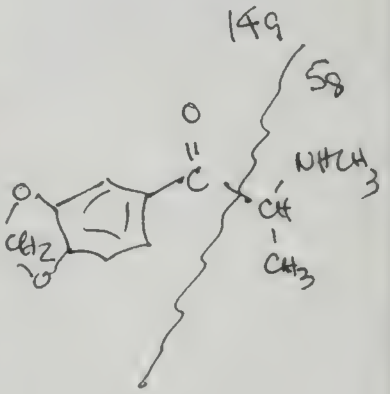
MW 259

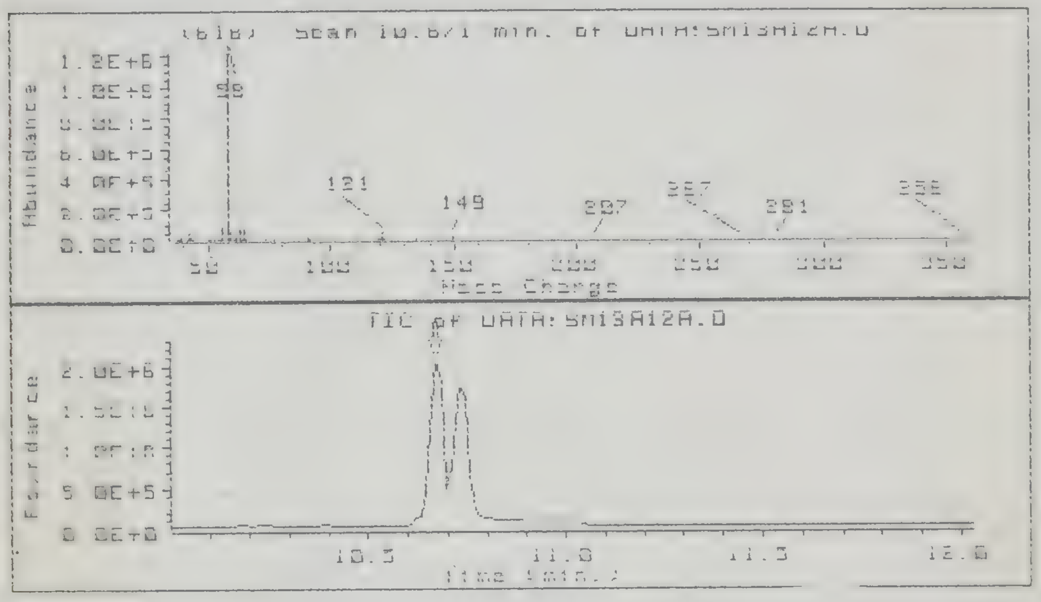
Dane phone calls
#2 April 14 1995 - OK -
he will alert me re
Pablo sources.
$110 for Micro analyses.

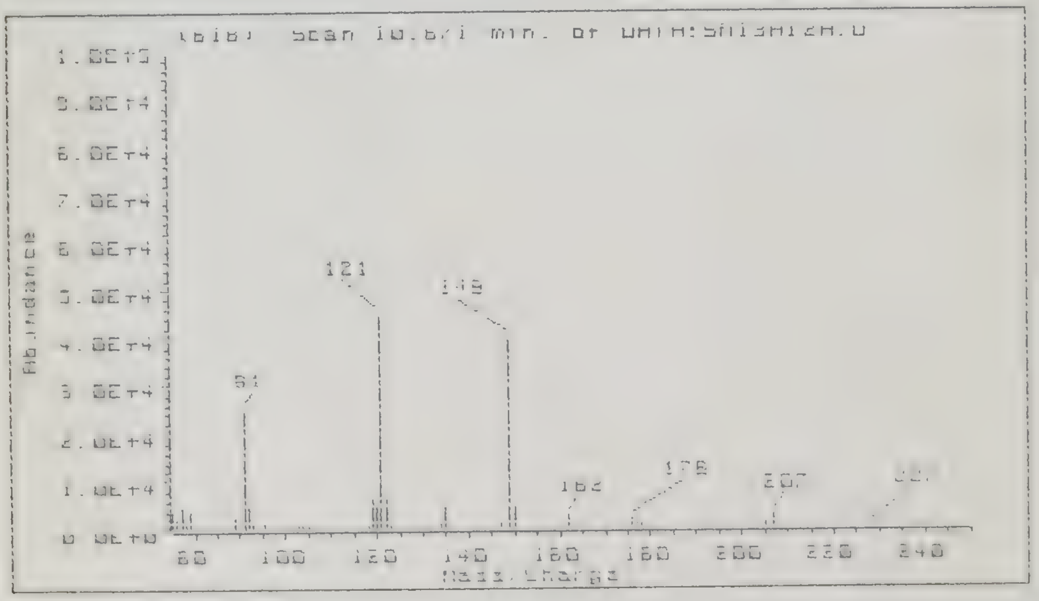
(10) from @ methylone GCMS



MW 207

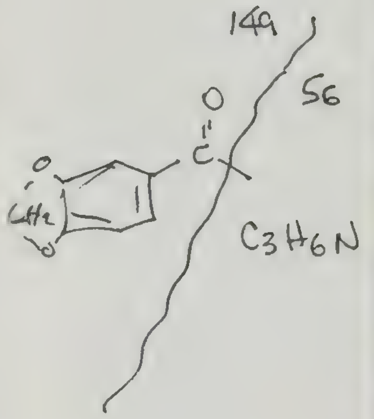


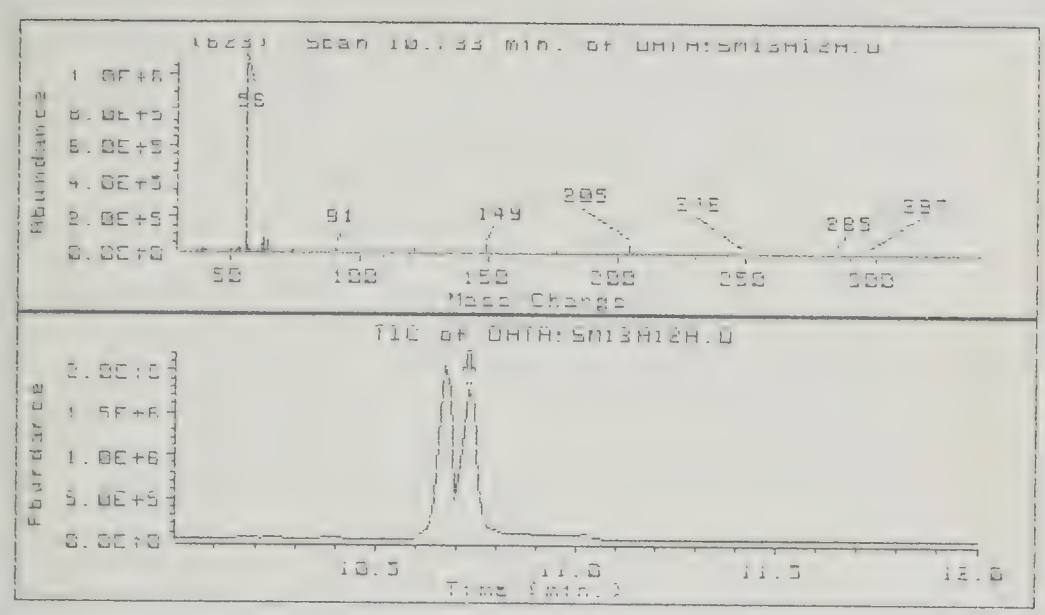


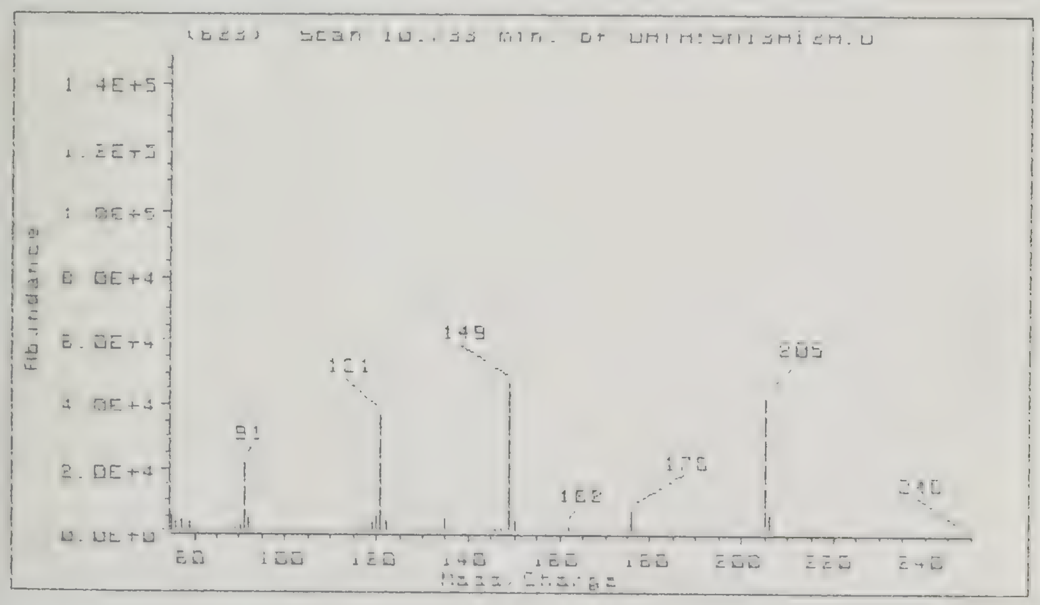


(11)

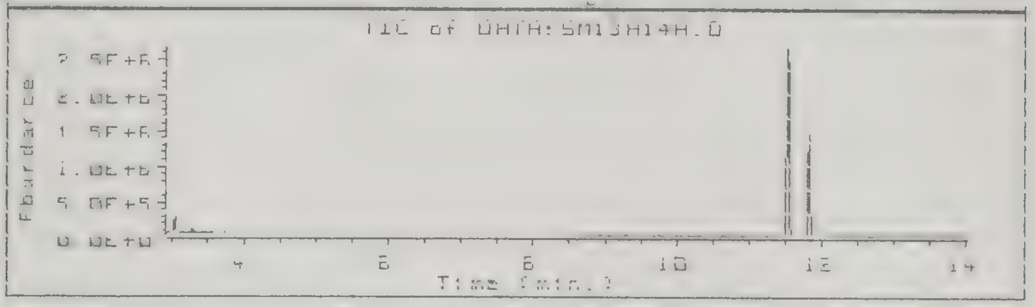
MW. 205

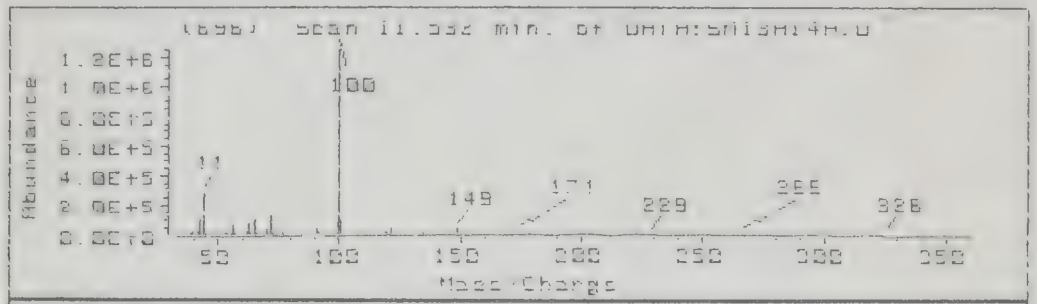

149
56
O
C
C_3H_6N

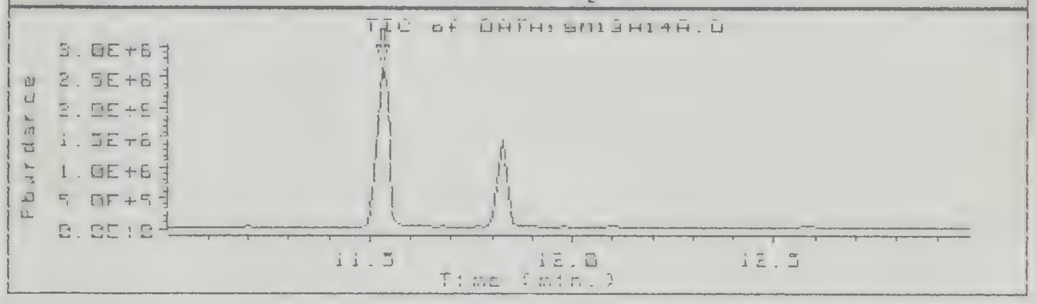

Scan 10.33 min. of DATA:SMI3HI2H.D
Abundance
Mass/Charge
TIC of DATA:SMI3HI2H.D
Time (min.)

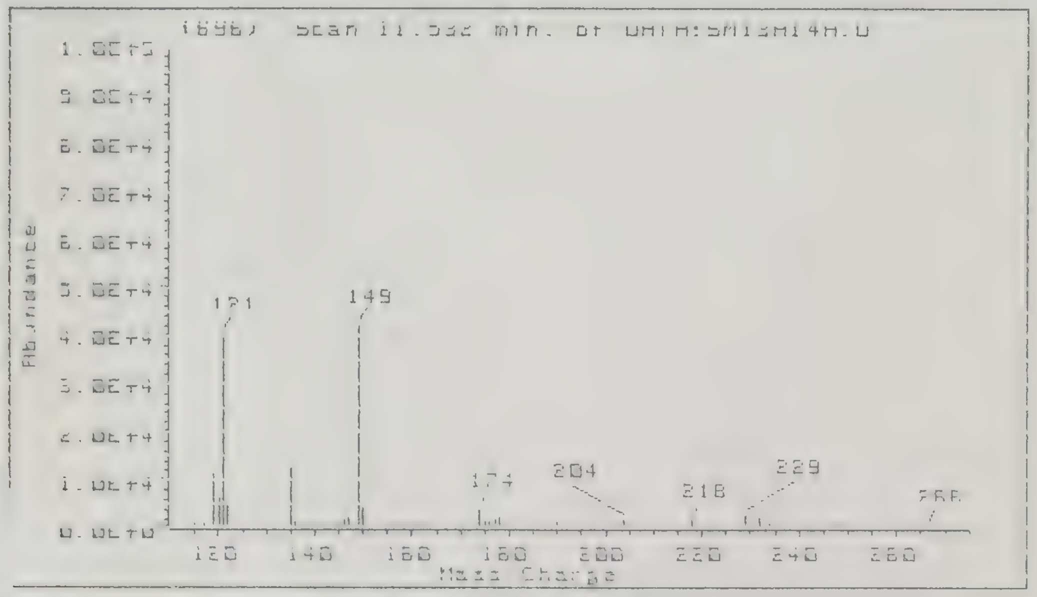

Scan 10.33 min. of DATA:SMI3HI2H.D
Abundance
91
121
149
162
176
205
Mass/Charge

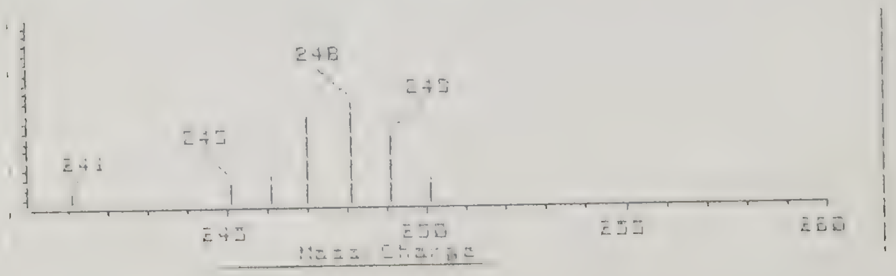
(12) DIETHYLONE · See page 9



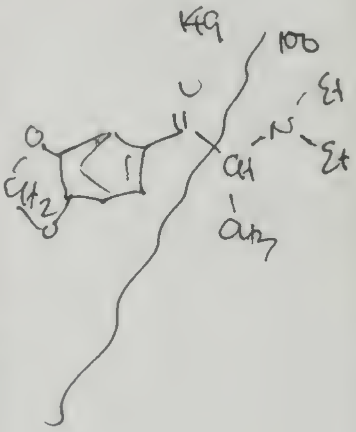


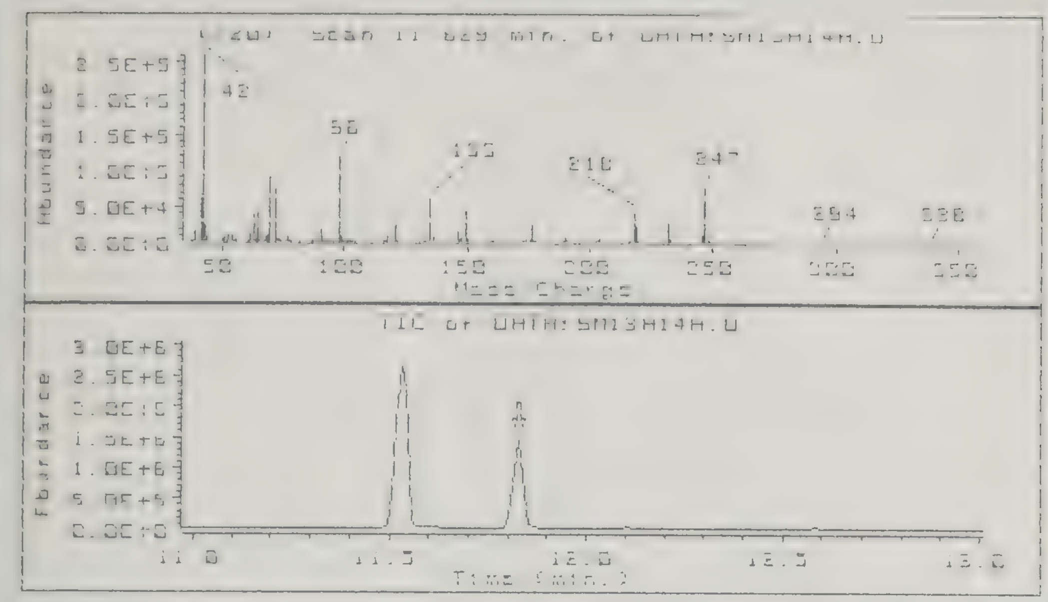


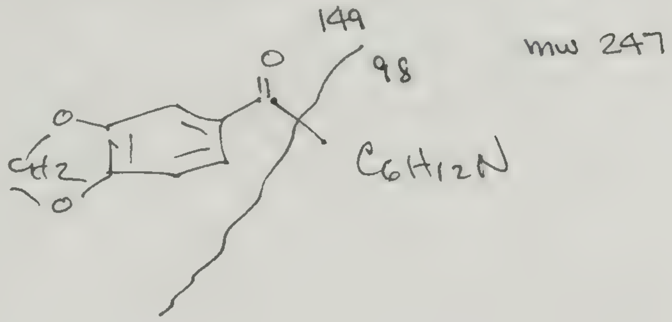




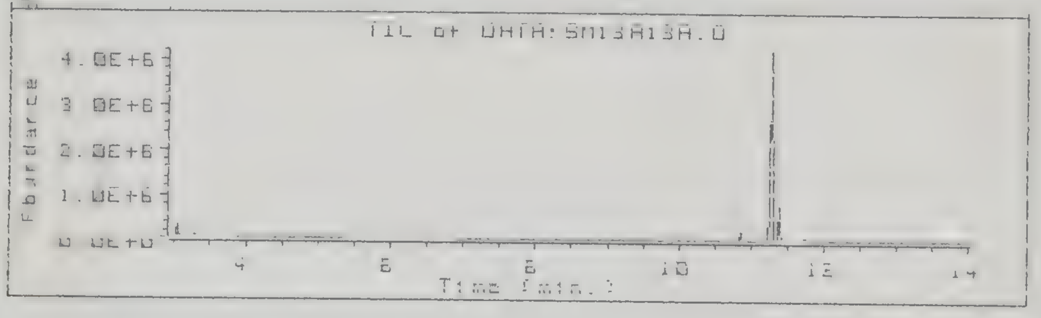
mw 249



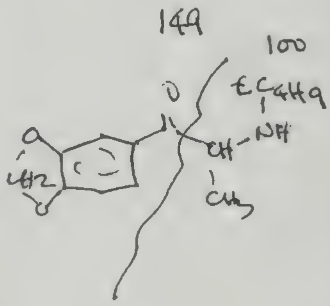

Abundance
Mass/Charge
TIC of DATA:SM13A14A.D
Abundance
Time (min.)

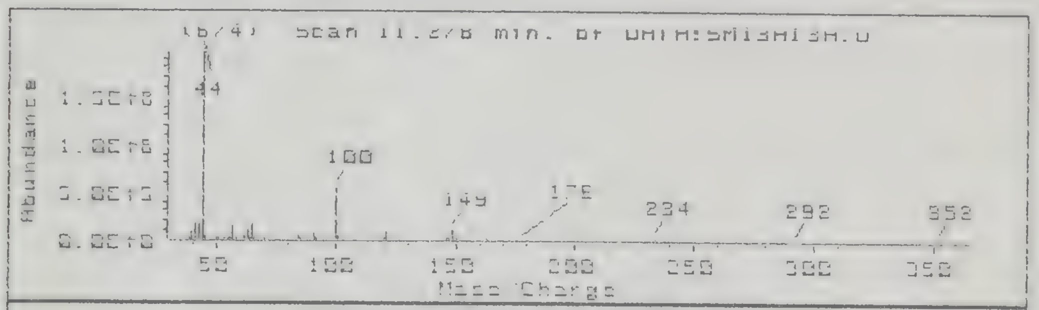

149
98
C6H12N
CH2
mw 247

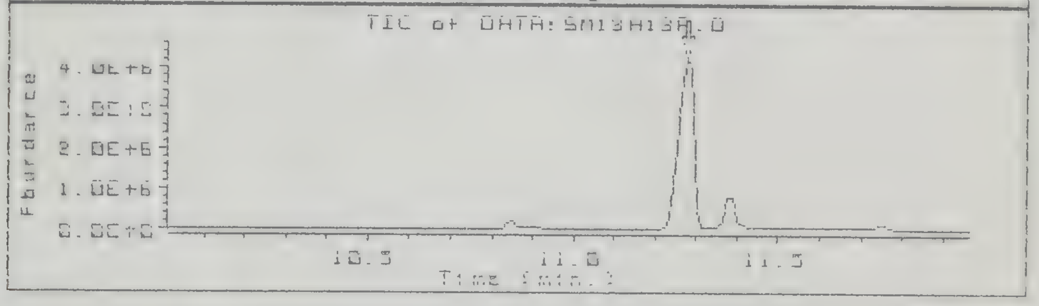
(14)

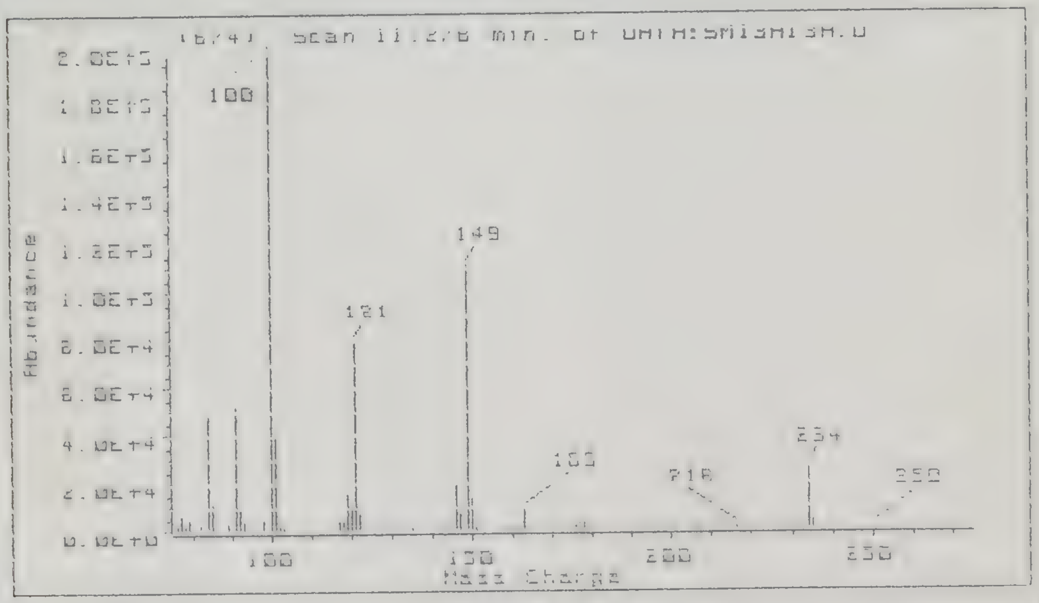

TIC of DATA:SM13A13A.D
Abundance
4.0E+6
3.0E+6
2.0E+6
1.0E+6
0.0E+0
4
6
8
10
12
14
Time (min.)

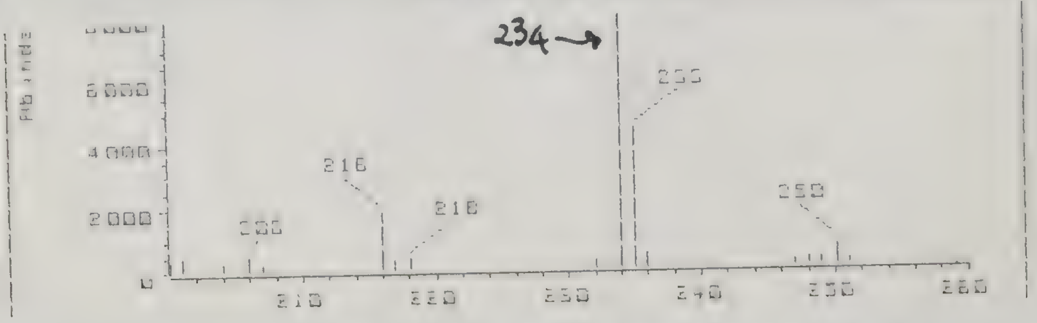
MW 249

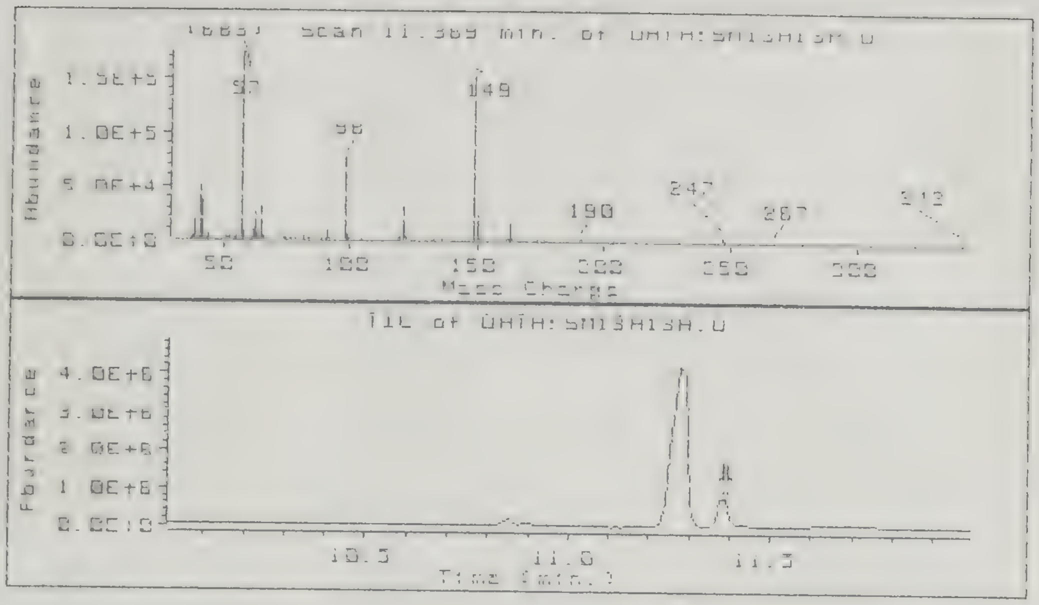

149
100

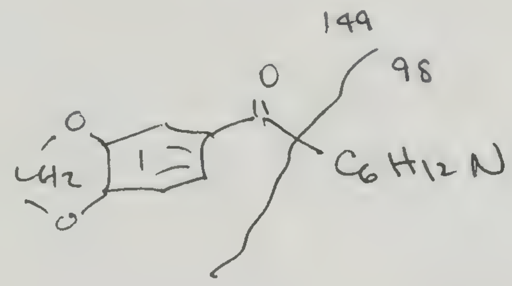

Scan 11.276 min. of DATA:SM13A13A.D
Abundance
1.5E+6
1.0E+6
5.0E+5
0.0E+0
44
100
149
178
234
292
352
50
100
150
200
250
300
350
Mass/Charge


TIC of DATA:SM13A13A.D
Abundance
4.0E+6
3.0E+6
2.0E+6
1.0E+6
0.0E+0
10.5
11.0
11.5
Time (min.)


Scan 11.276 min. of DATA:SM13A13A.D
Abundance
2.0E+5
1.8E+5
1.6E+5
1.4E+5
1.2E+5
1.0E+5
8.0E+4
6.0E+4
4.0E+4
2.0E+4
0.0E+0
100
121
149
163
218
234
250
100
150
200
250
Mass/Charge

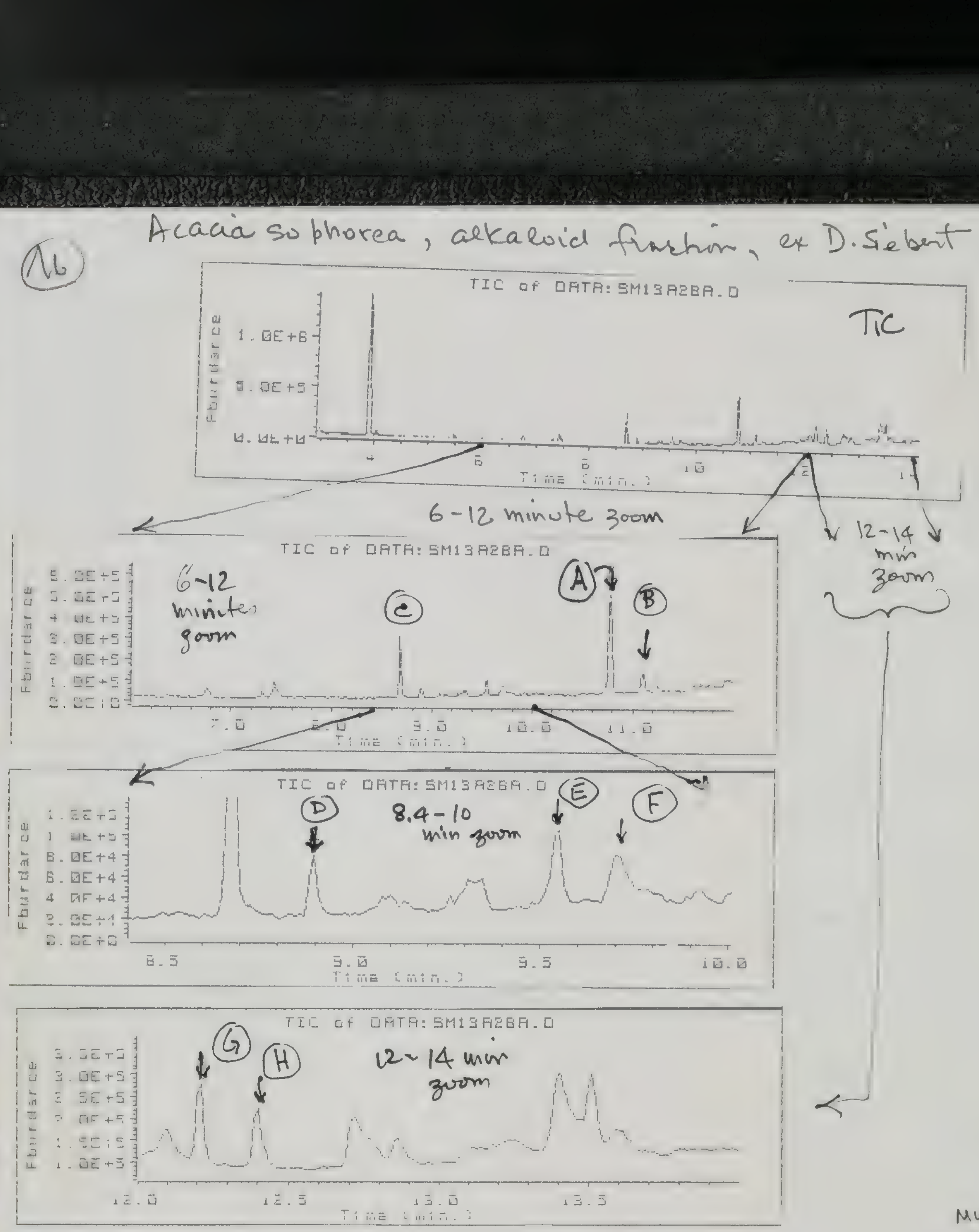

Abundance
6000
4000
2000
0
234 →
235
216
218
206
250
210
220
230
240
250
260

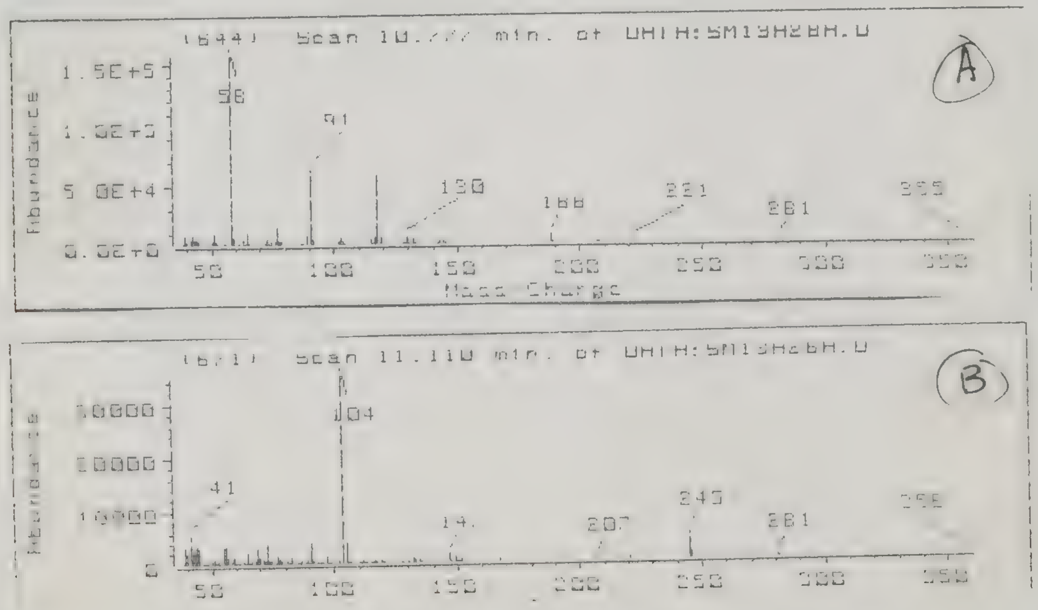

Scan 11.369 min. of DATA:SMISHISH.D
Abundance
1.5E+5
1.0E+5
5.0E+4
0.0E+0
57
98
149
190
247
287
312
50
100
150
200
250
300
Mass/Charge
TIC of DATA:SMISHISH.D
Abundance
4.0E+6
3.0E+6
2.0E+6
1.0E+6
0.0E+0
10.5
11.0
11.5
Time (min.)

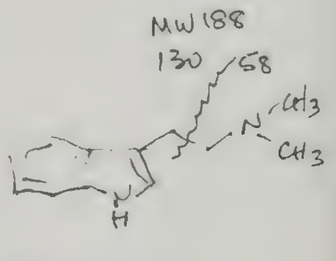

149
98
O
C6H12N
CH2
O
O

(16)

Acacia sophorea, alkaloid fraction, ex D. Siebert

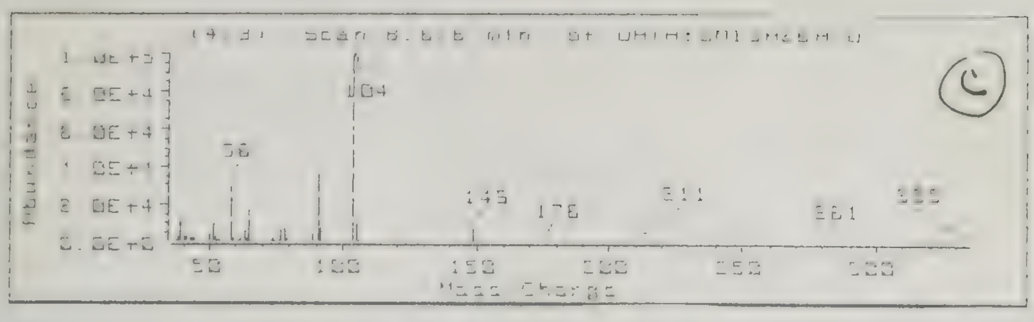






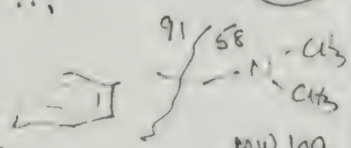
DMT

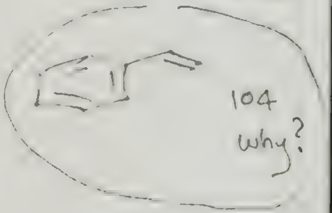
(17)

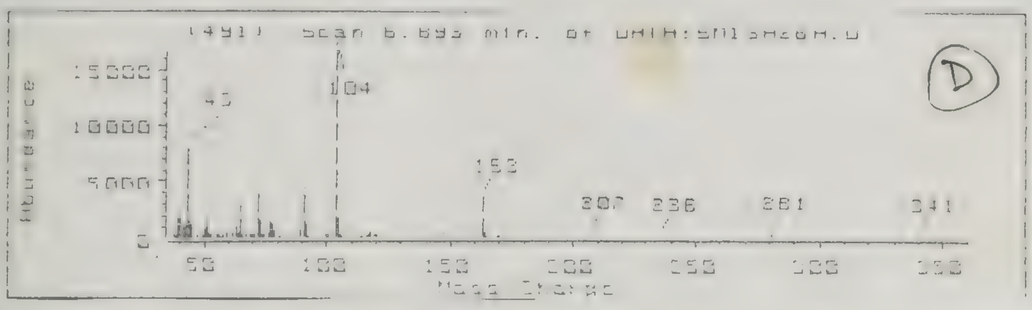


???

← 149





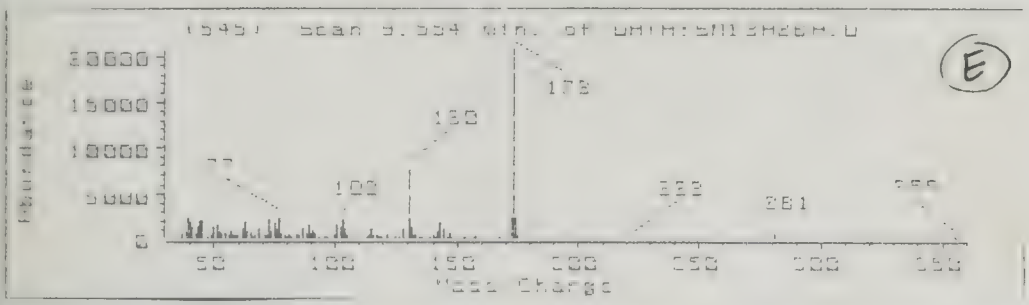


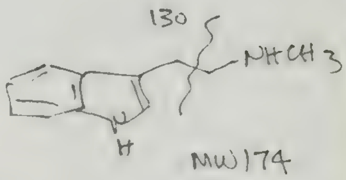
???

← 163

MW 163

(= 149 + 14)

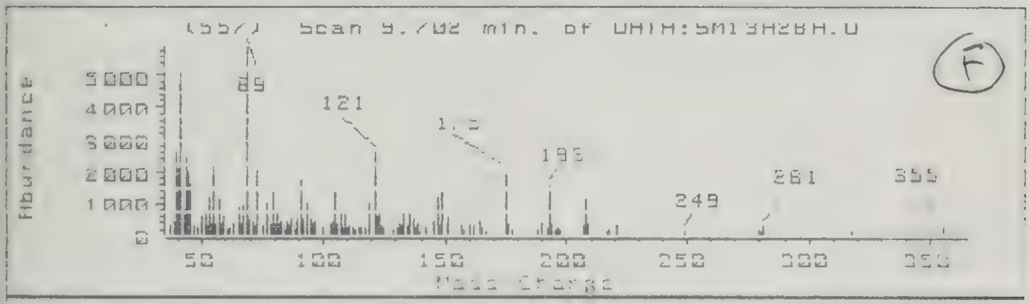


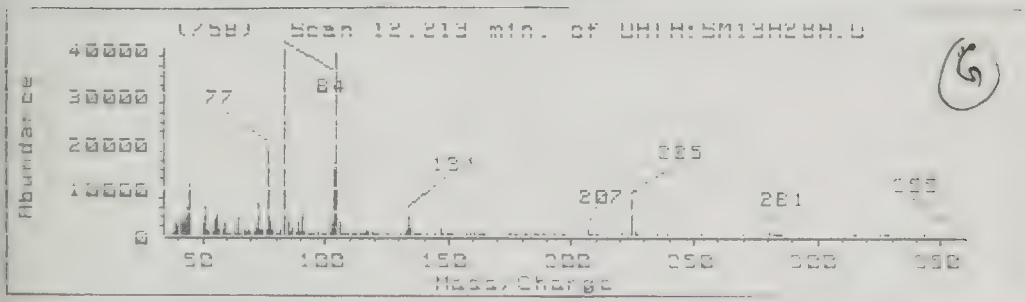


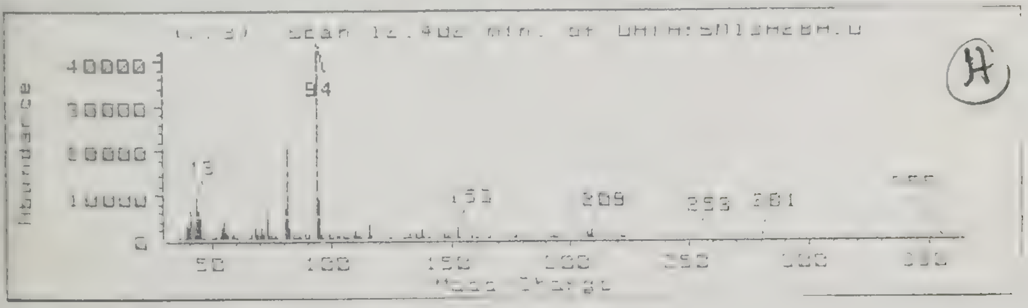
MMT

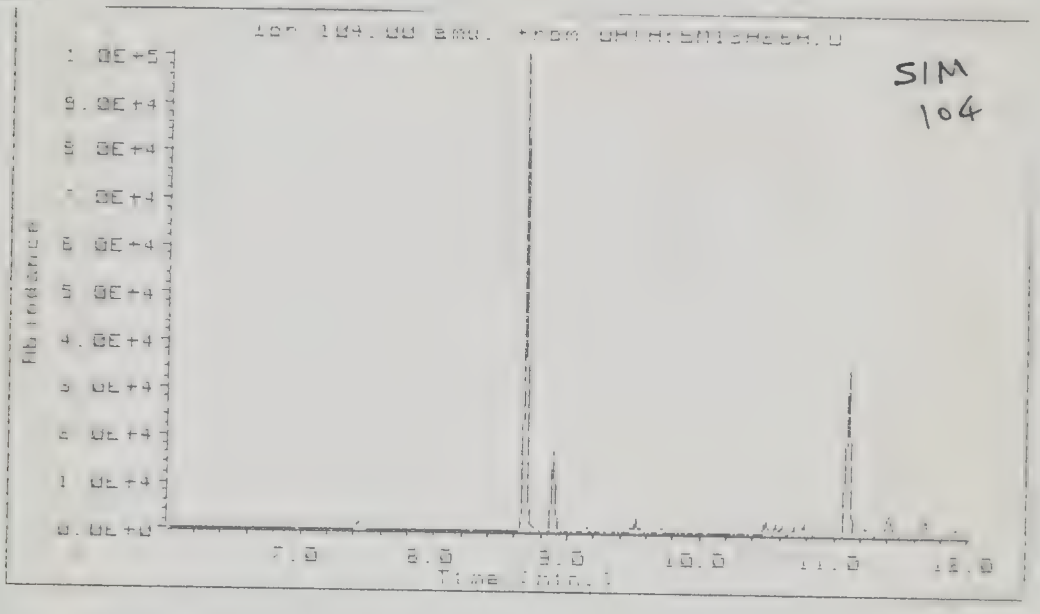
MW 174

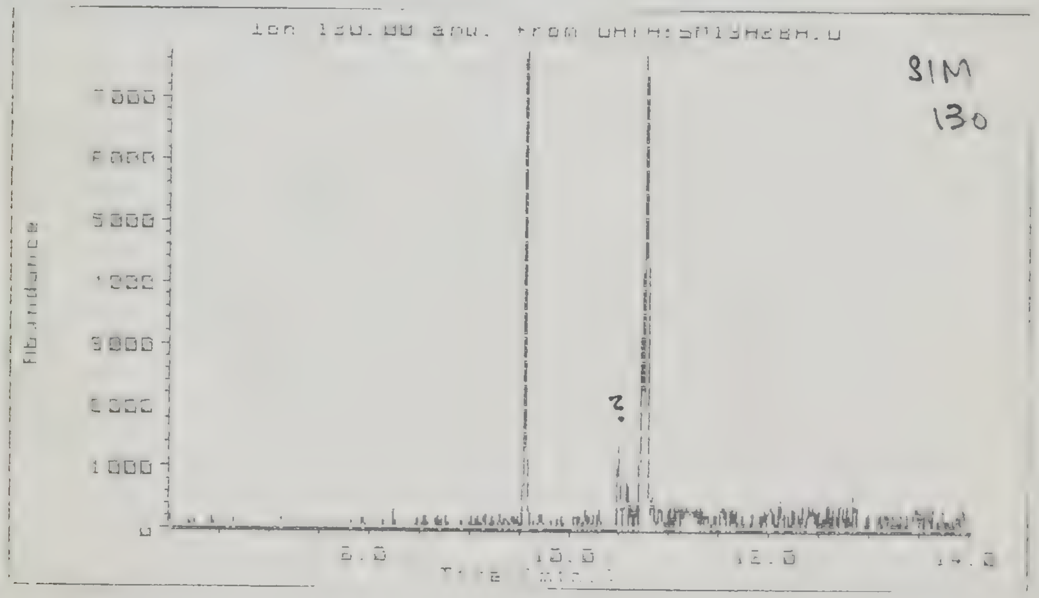
P-1 = 173





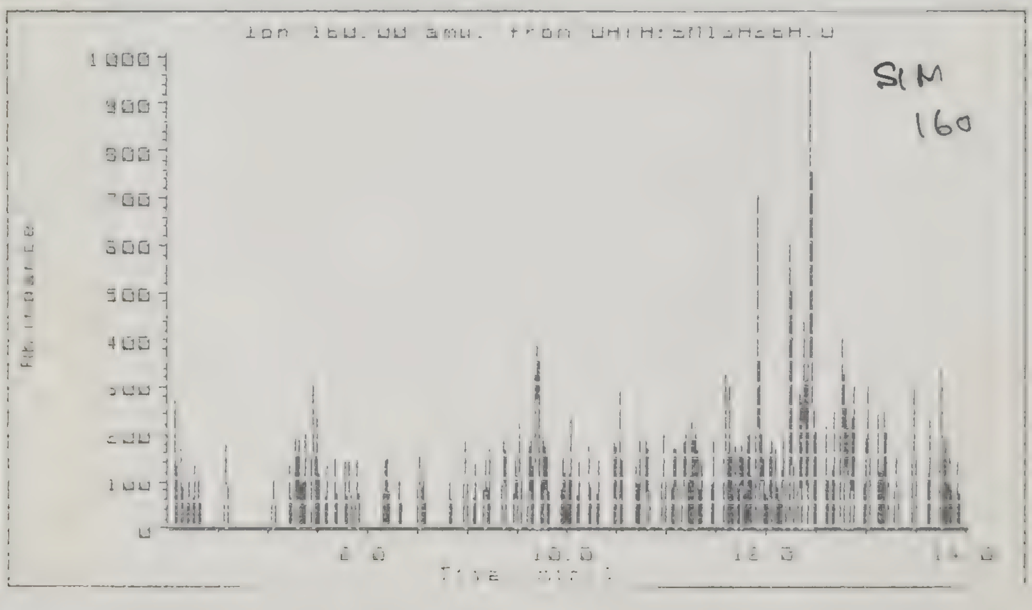




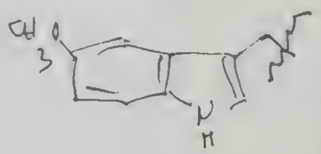


MMT
DMT

probably no other indoleamine



no hint of



∴ no 5-MeO-DMT
5-MeO-MMT

120
12
48
180
12
16
21 8

10 g tryptamine – add
10 g Butyl formate
Δ to reflux in RB – mantle – 24 hrs → dark, clean solution.

19.2g crude

Strip on RE → 19.2g viscous oil.
into 250 ml H_2O.
acidify c̄ HCl (stuff in blue-top NOT HCl)
(big 6 lb bottle OK)
xtrt 3 × 25 ml CH_2Cl_2
pool – wash 1x dil HCl. 50 ml.
wash 1 × 5% NaOH, 50 ml

11.5g crude

Strip on RE. to hard vacuum → 11.5g black oil.
onto KR. Vac to 0.05 mm. distil
220-240° over – bad vacuum tubing?
apricot color. Still stuff in pot.
push to 250° – no residue in pot.
9.0 g drained out of receiver – orange oil –
not xtal ON – some wall oil → xtal.

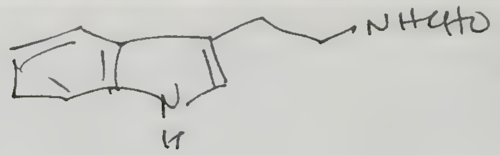
115° nothing.
135° .05 mm. nada
150°
165°
180°

9.0 g over.
Δ (flame)
0.05 empty

let stand – very hot weather – very slow xtals.
GCMS shows some unreacted tryptamine –
and, strangely – hints of di-CHO'ing.
a week later – slow growth of more xtals
Spectra pages (20, 21)

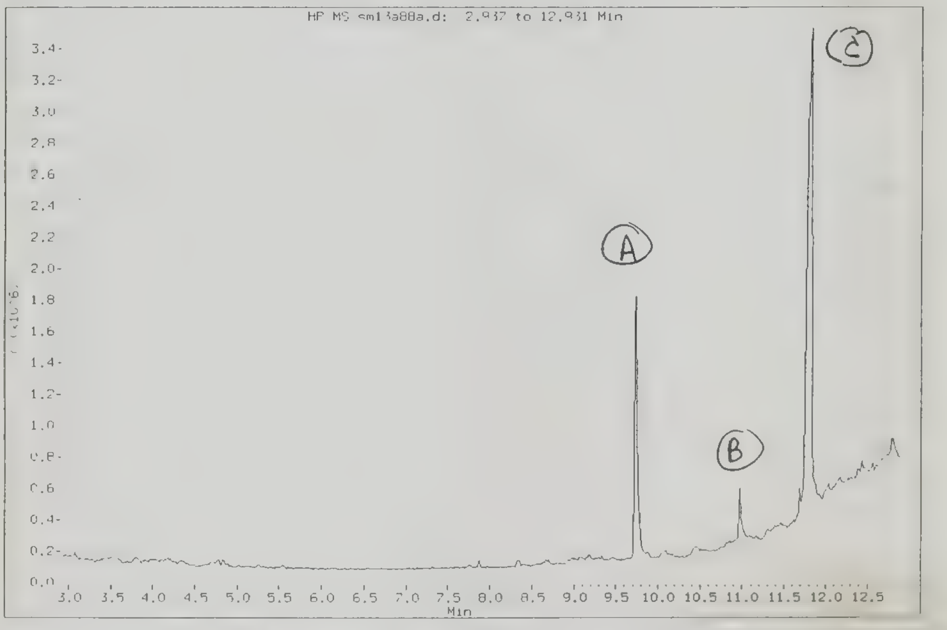
Add ~30 ml Methyl formate –
reflux ON – Mass Spec. now a single formate peak – BUT
a giant at 3 minutes? strip hard → 7.7 g. KR

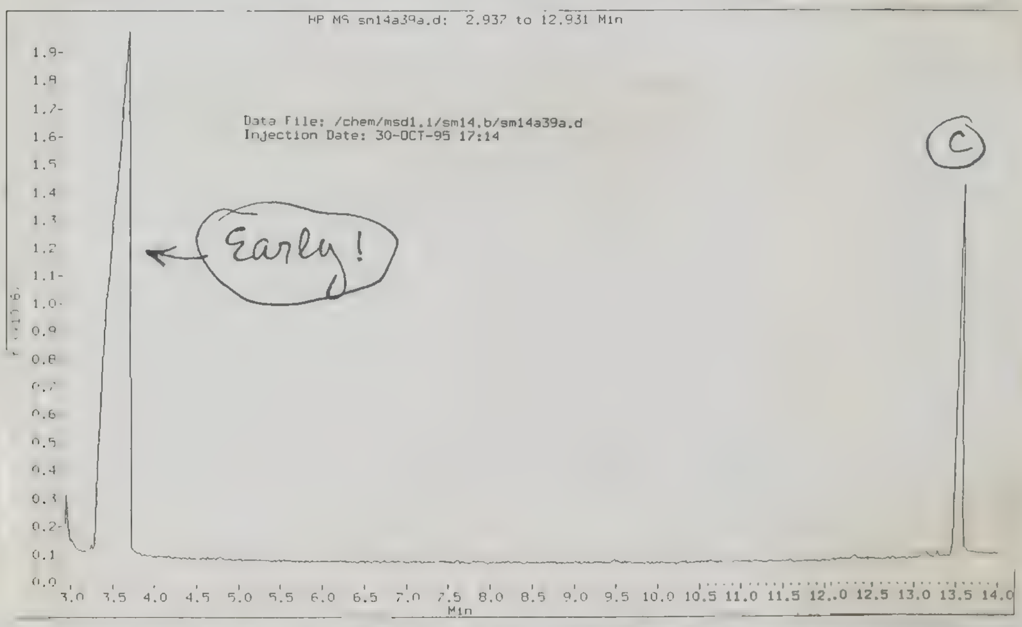
170° start,
190° done
0.1 mm
} → 6.87 g pale yellow oil

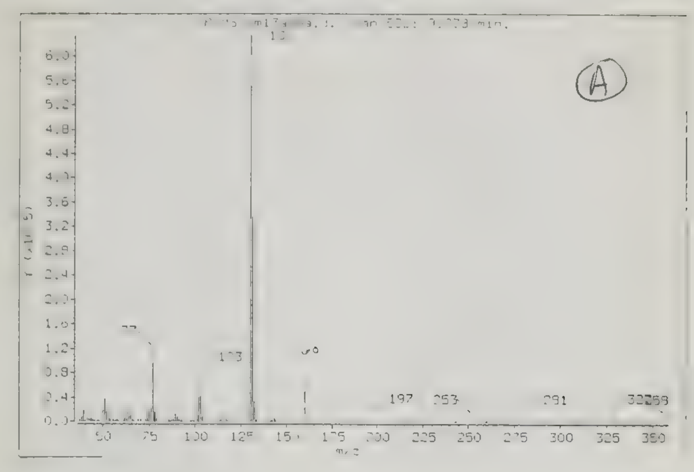
Spectra of  from page 19.

Crude, slowly crystallizing yellow oil, from page (19)

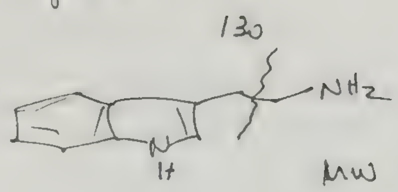
Then, pure distillate - bottom page



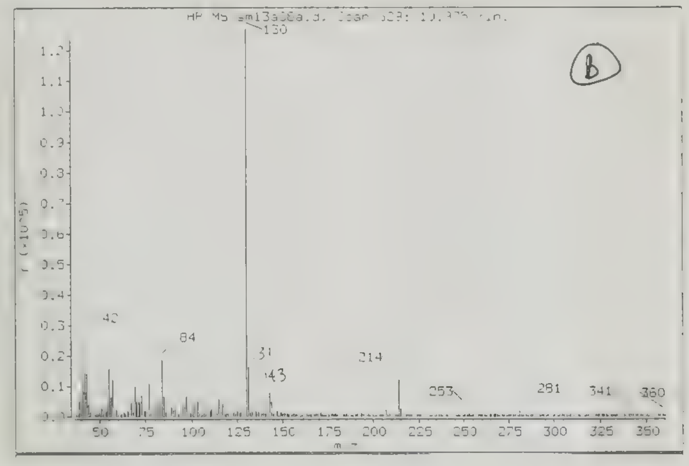




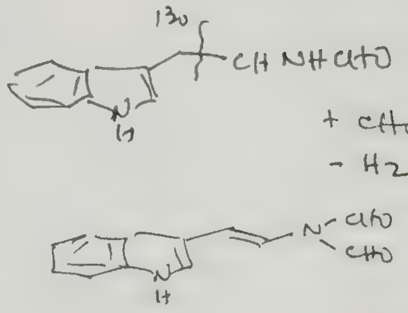
Tryptamine



MW 160



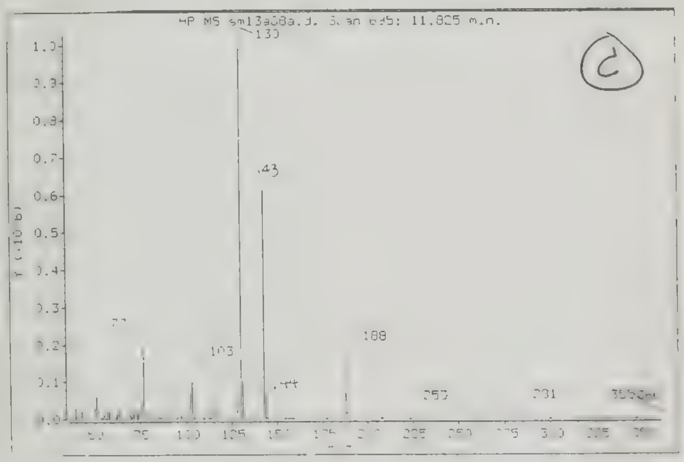
WEIRD



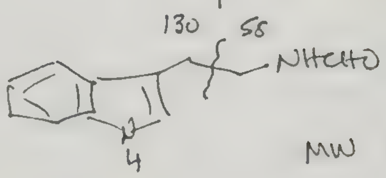
+ CHO
− H2

MW 214

OOO?



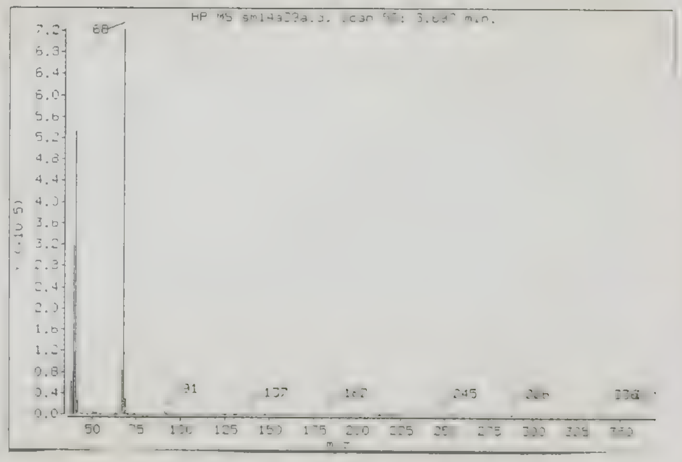
N-formyl tryptamine



MW 188

early! →

???



In a RB 3 neck flask - Argon - stirrer, reflux, good gas flow.
Add 60 ml 1N LAH in THF. at room temperature. (60 mM)
Make a solution of 1.88 g formamide in ~ 40 ml anh. ether.
Δ LAH to near reflux, add ether solution dropwise.
2 fold excess of LAH at most generous.
Up to reflux in evening, good stirring, Slow deposition of white surface scab - AM - still reflux (ether? not THF) and a lot of white solids.
Remove a squirt of the soluble for GCMS analysis →

AM - to RT. 24 hrs later - kill with
20 ml 50% aq. THF. no more fizzle.
filter, wash c̄ 4 x 25 ml damp THF.
check pH of filtrate - damp pH paper. BASIC
Evap filtrate + washes to dryness in rot. evap.
→ 1.39 g pale oil. Waiting to decide to acid - base - start of spontaneous xtals - save seed -

Distill at KR

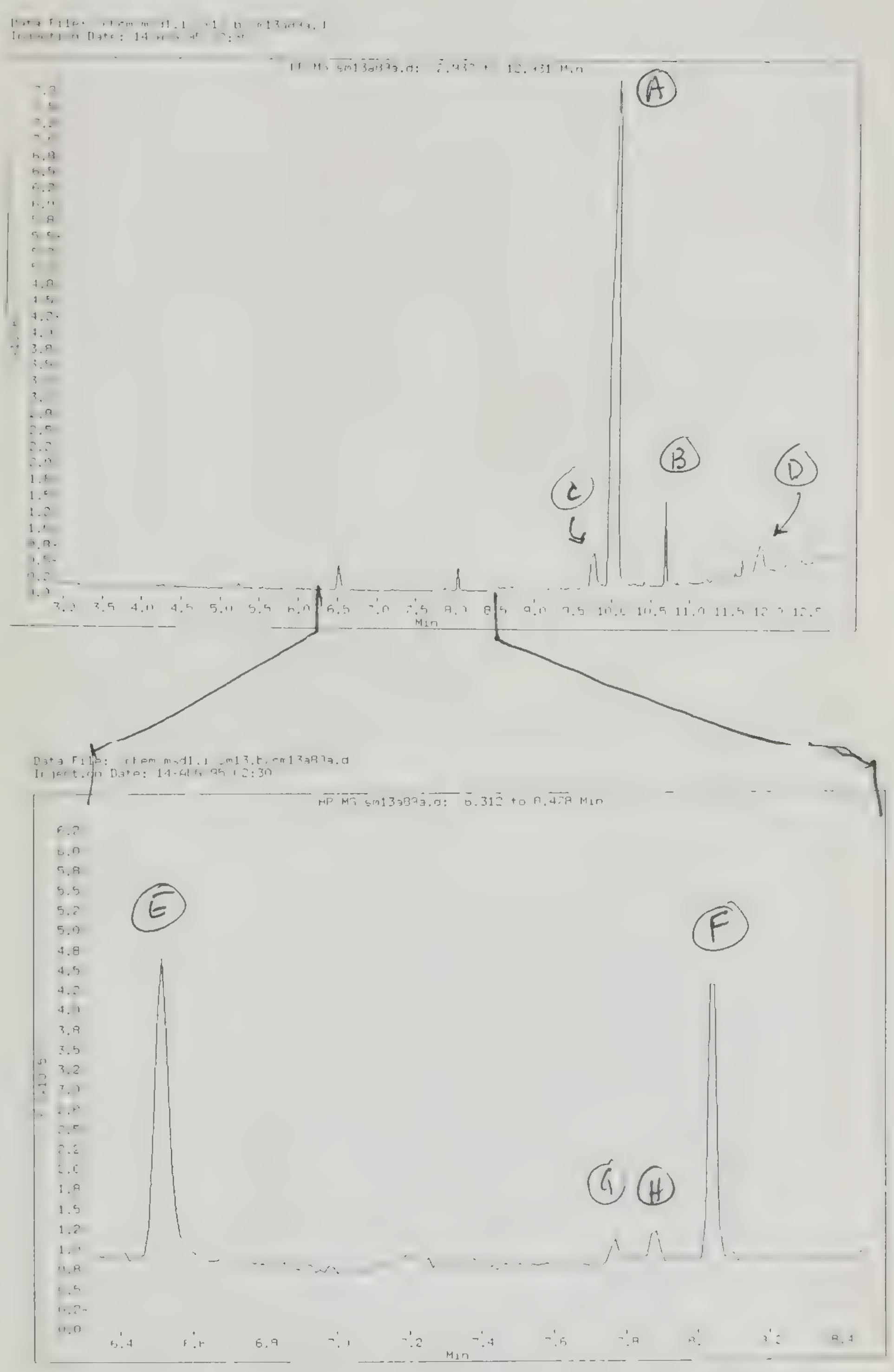
0.1 mm Hg
60° no
110° blush
120° more blush
135 - 145° over, white oil.
1.22 g - short. & immediate xtals to white solid.

~~MMT~~ NMT

Conversion to .HCl — Manske - base mp 90°, .HCl mp 180°
0.22 g base (no mp taken) (turning rusty brown) + 1 g IPA
Δ puts it into solution. add conc HCl - each drop → green-blue color that dissipates on stirring - when acidic - color stable - no xtals - add ~ 1 ml ether → cloudy - stir - scratch → xtals
filter, IPA/ether wash, then ether wash - dry to constant weight

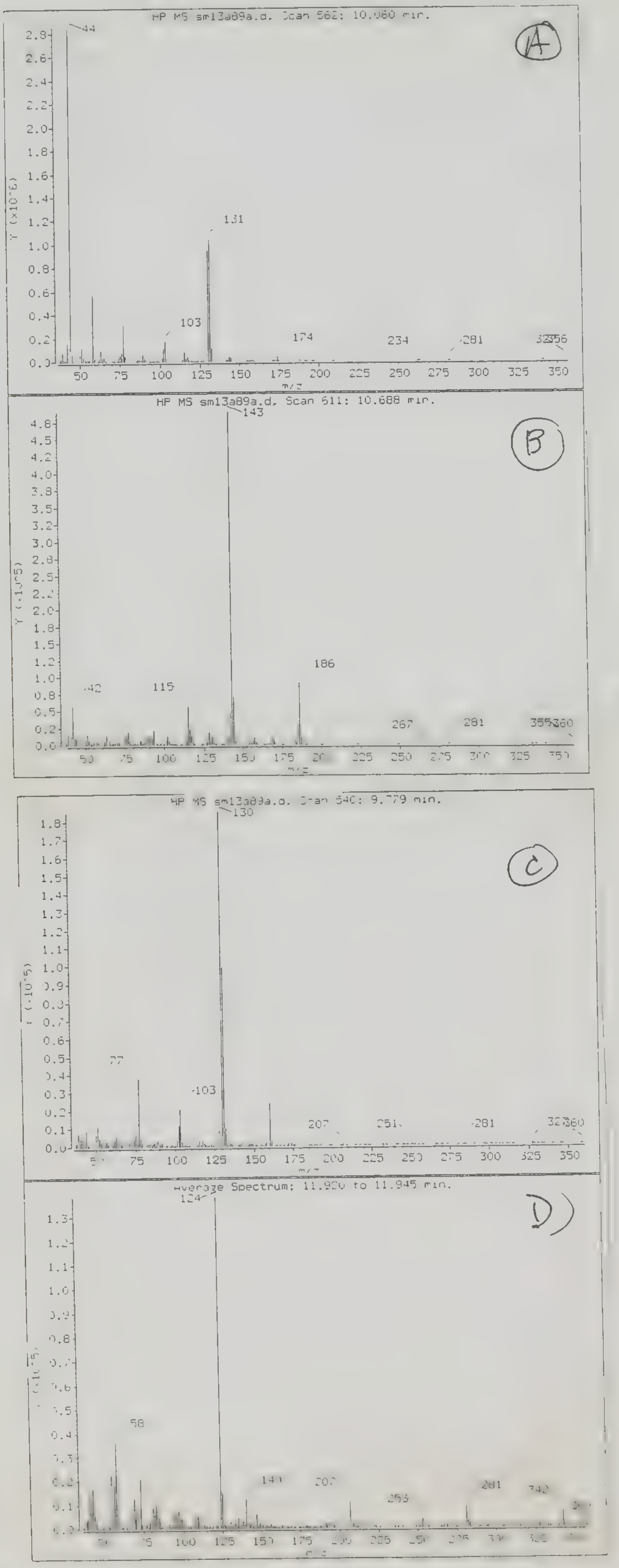
0.176 g. off-white xtals. (blue tinge) or (grey tinge)
mp 174-6°

GCMS of crude, solubles, of 22.



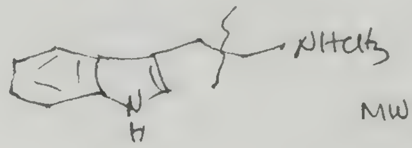
See separate analysis of (A) on page 26

from page 22 - 23 crude MMT



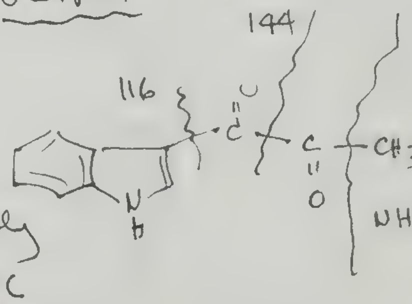
N-MT
~~MMT~~

130



MW 174

Weird

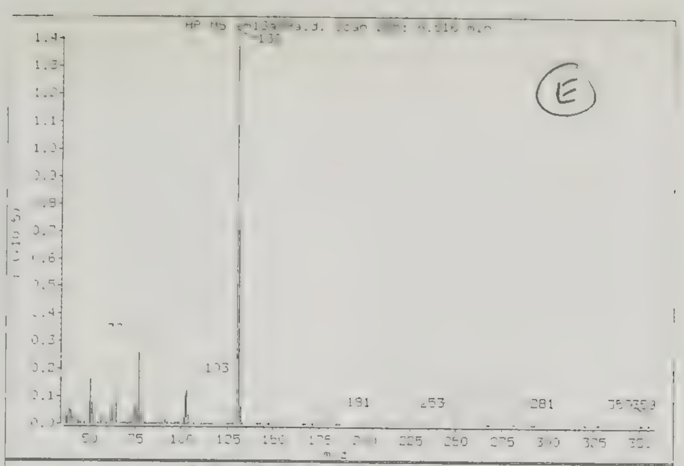


MW
187
188

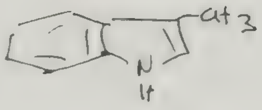
probably
N-Me THβC
See page 35.

tryptamine

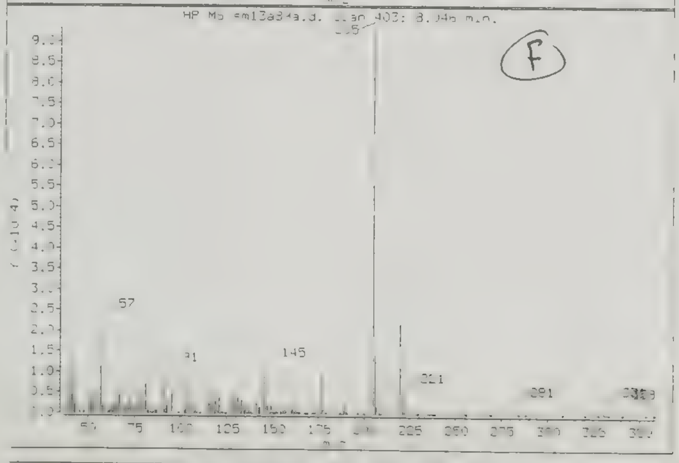
See page 21



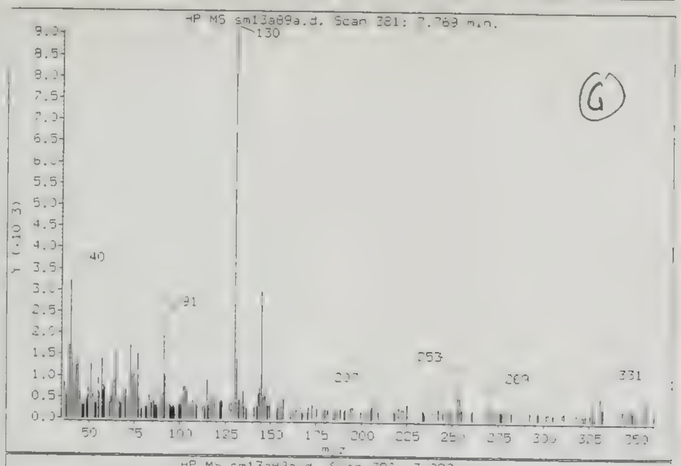
Skatole ?



MW 131

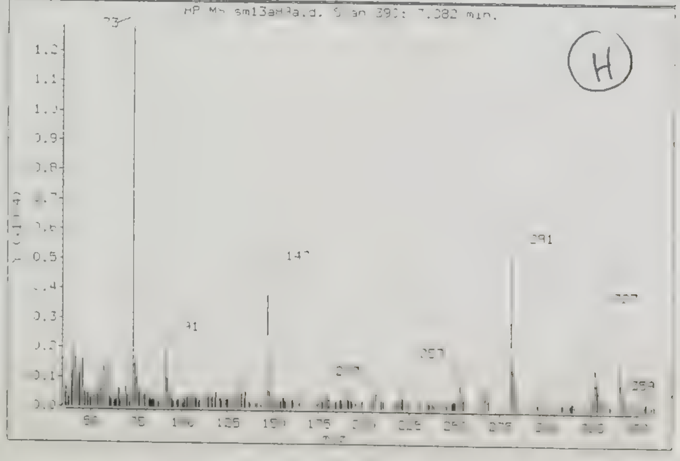


?



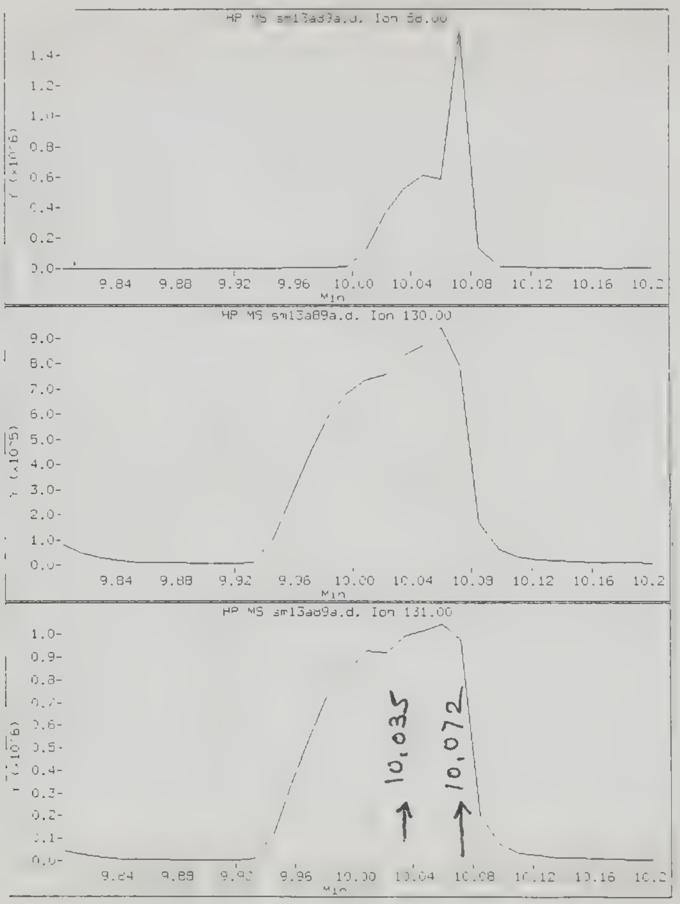
dimethyl -
ethyl - } tryptamine.

MW 145



?

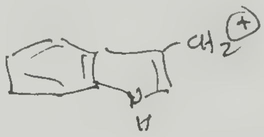
looking for complexity in peak A, page 23



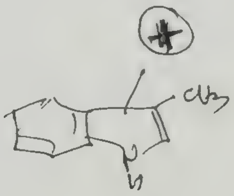
DMT

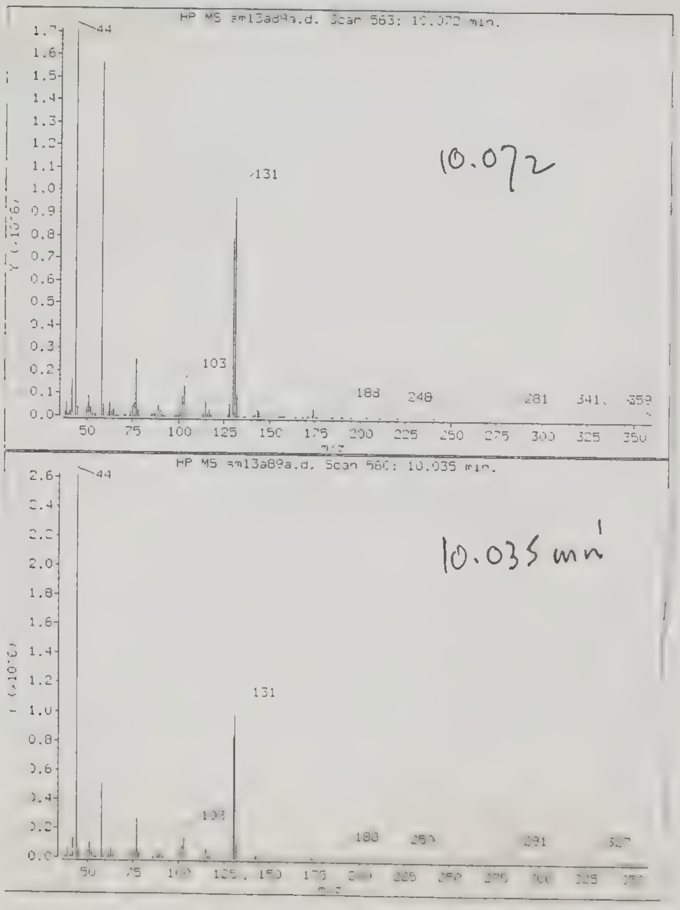
ion 58 $CH_2=N^{+}(CH_3)_2$

ion 130



ion 131

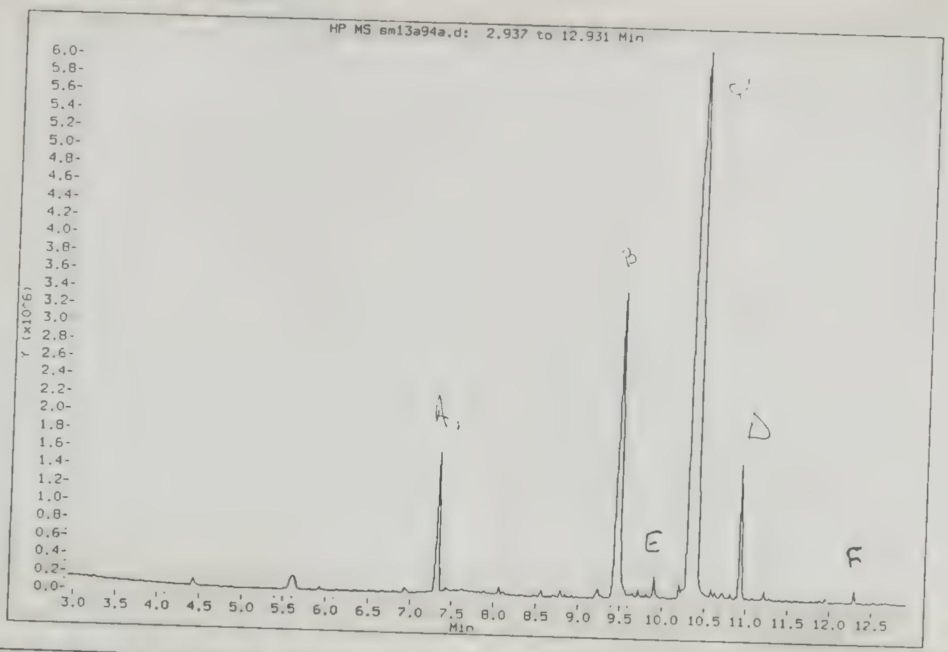


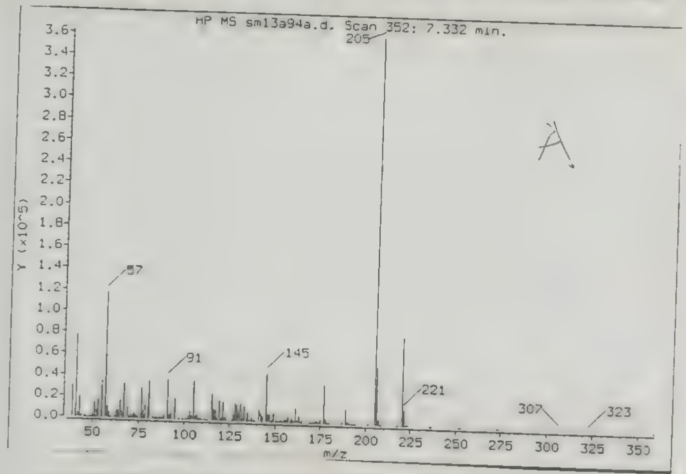


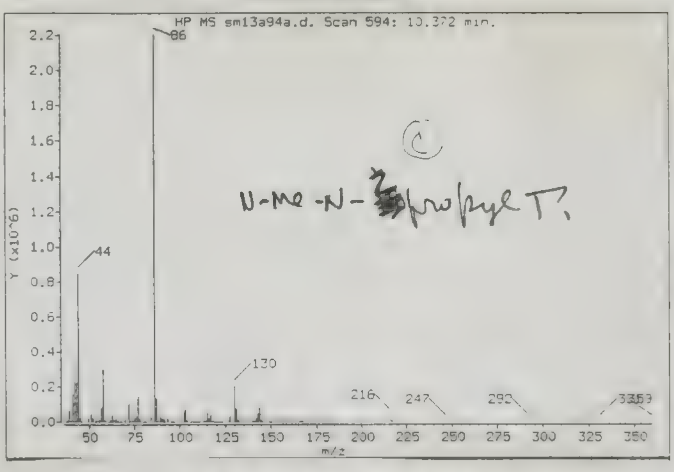
at SF.

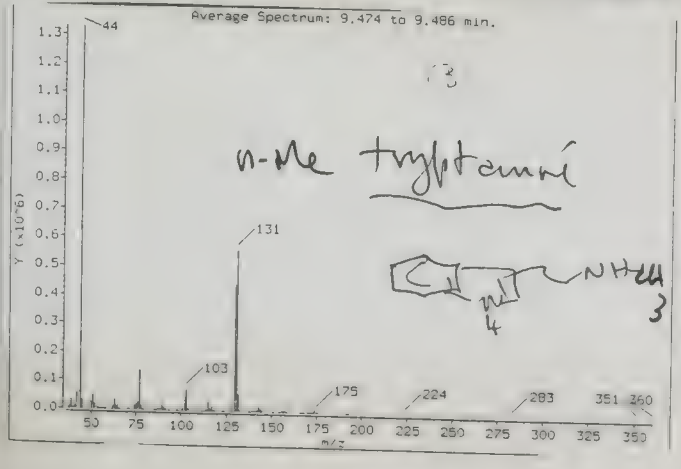
add neat propyl iodide to a few milligrams of MMT - heat 100° 1 hr → GCMS that says 4/5 propylated, some trace Pr_2 (= N^+(Pr)(Pr)(Me) & cracking) OK back.

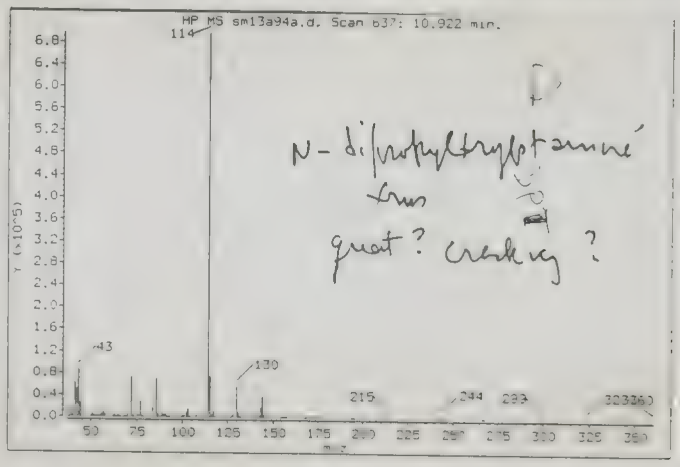
Data File: /chem/msd1.1/T2519/T2519/sm13a94a.d
Injection Date: 05-SEP-95 07:11











28

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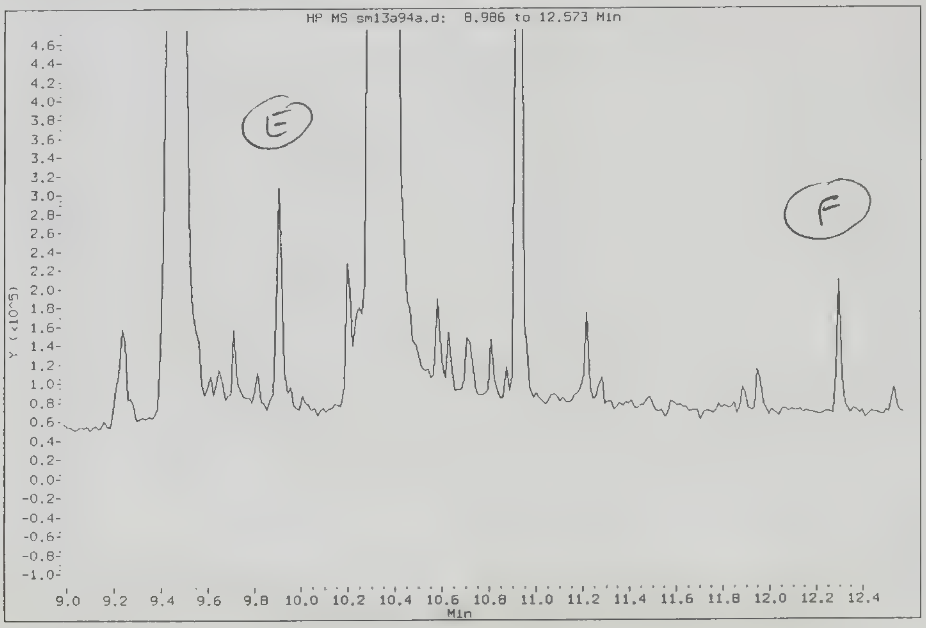
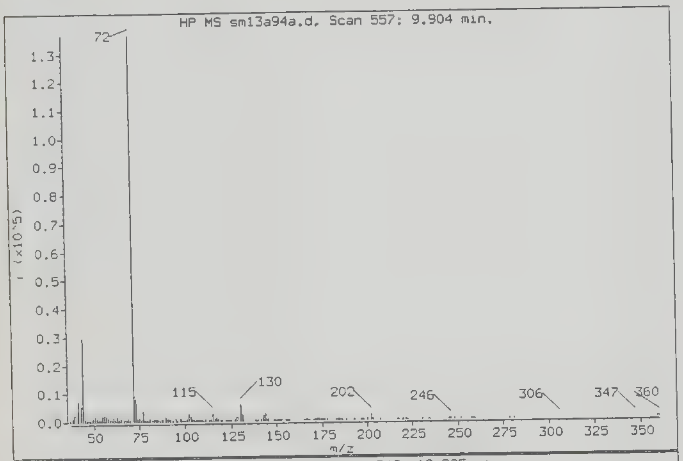
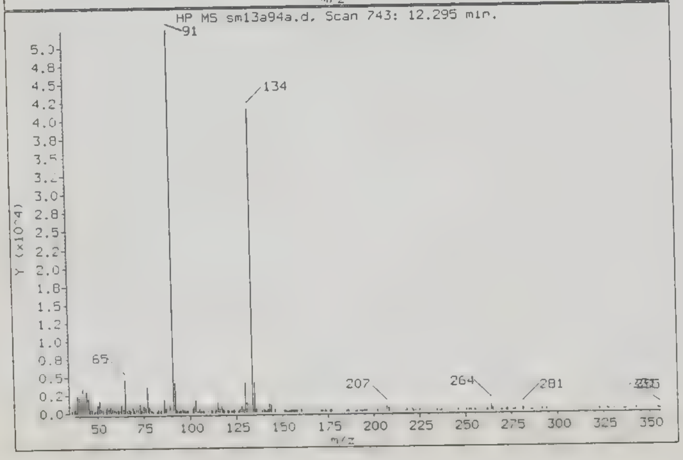
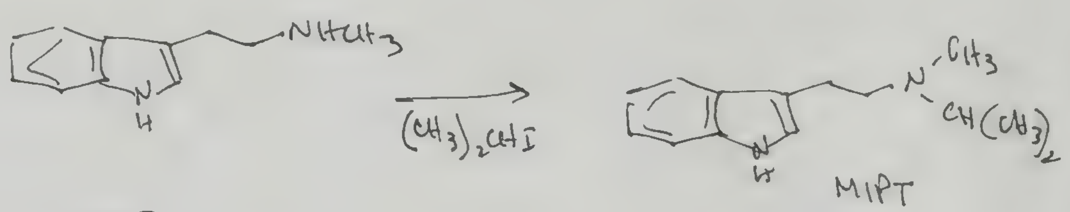






31

 attempt:



MIPT

0.3 g free base NMT ~~MMT~~ (1.22 g batch, page 22)
dissolve in 4.5 g IPA - slow to dissolve RT, color goes in first - ∴ maybe good as recryst. solvent.

1.2 g isopropyl iodide (4 x stoic) SB 10 hrs.
TLC 95/5 CH_3CN NH_4OH → part done (well separated)
50/50 CH_2Cl_2, EtOAc terrible.
add;

1.5 g more IP iodide - SB 15 more hrs. - done (largely). no spot at origin (no quat?)

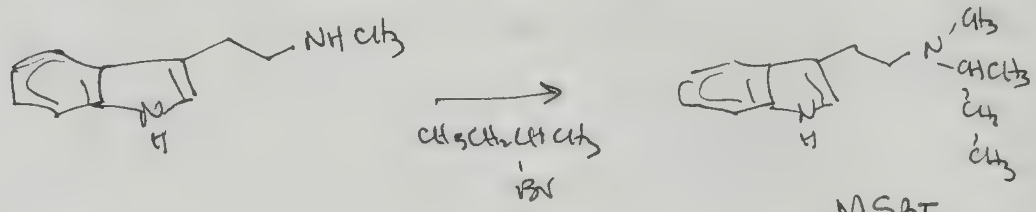
Strip to residue - suspend between 50 ml CH_2Cl_2 and 25 ml 5% NaOH - all goes in - color mostly to CH_2Cl_2 - separate - xtract base c̄ a little CH_2Cl_2 - pool - wash c̄ ~5% sodium bisulfite soln - some, not all, color goes. once more c̄ 5% base - flash → 0.36 g black oil for KR'ing.

Distill at KH, which distills between 150-160° → ~ white oil - will not crystallize
0.19 g very viscous.

100 flash
135 - (very little at this) many fits foTeg.
130
150 over.
0.05 mm/Hg

DR sample. 0.38 g excellent base 95% MIPT
5% almost NMT

(34) attempt:



MSBT

300 mg ~~NMT~~ NMT into
4.5 g IPA - dissolve c̄ crunching & swirling - add
2.4 g sec. Butyl bromide -
reflux 6 hrs ~1/4 done TLC
reflux 18 hrs more - essentially done.

Strip → colored oil - dissolve in 50 ml CH_2Cl_2 - add
25 ml 5% NaOH. shake separate. flash
→ 0.29 g crude

KR. ~~#~~ 150°-160° / 0.05 mm.
0.27 g white oil GCMS (Crop A) recycle

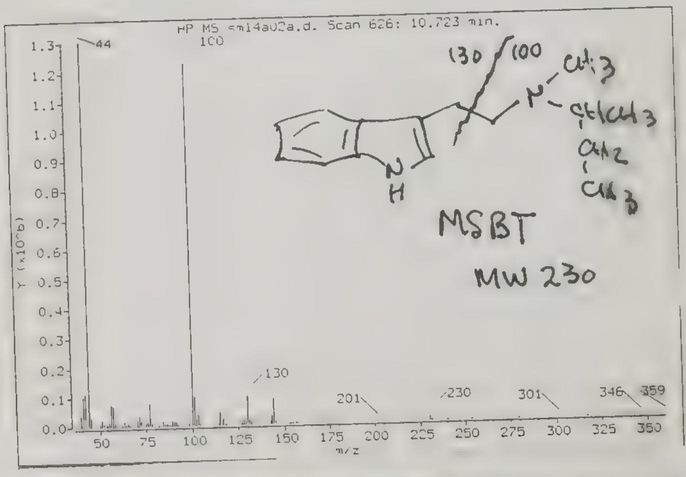
110° no ~~#~~ blush
140 about to start.

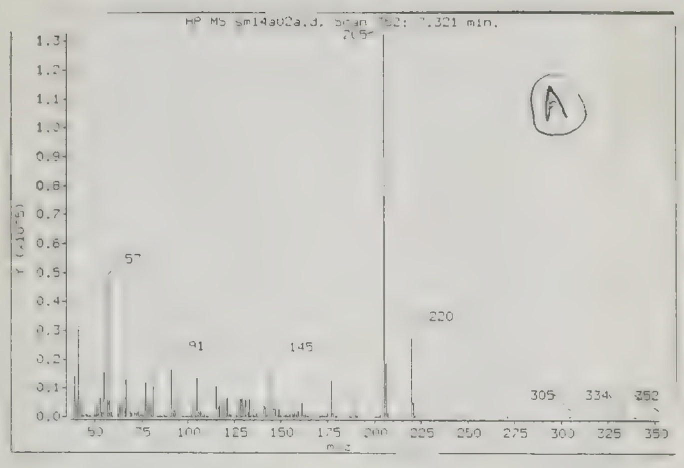
all back in RB flask.
0.27 g 65% stuff.
4.5 g IPA
2.4 g sec BuBr
0.63 g ~~#~~ g KI - onto SB. on - ~~#~~ 9 PM.
off 4 PM (19 hrs more)

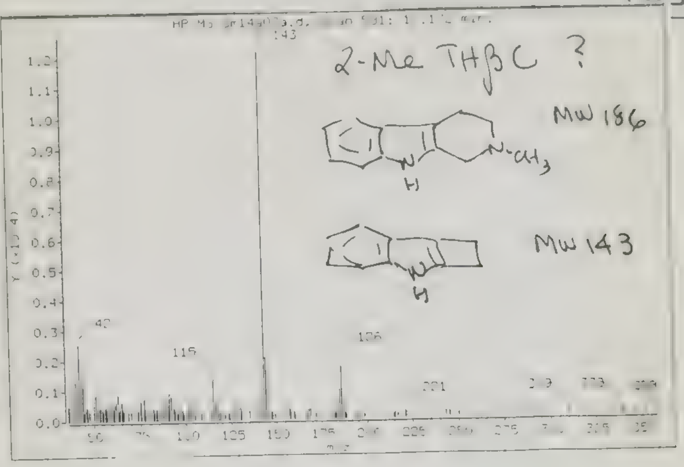
~~#~~ Very light colored liquid - KI did not dissolve.
this was GCMS'ed for
crop B ≥95% pure.

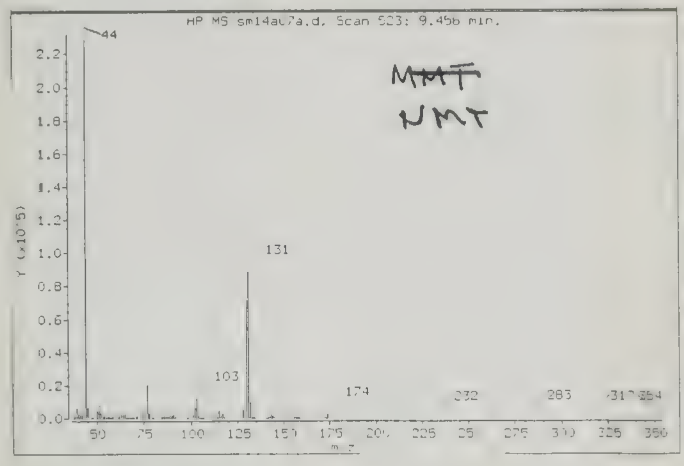
Strip - suspend between CH_2Cl_2 & dil base
Sep. wash c̄ H_2O - strip CH_2Cl_2 → 0.37 g pale oil - too fluid.

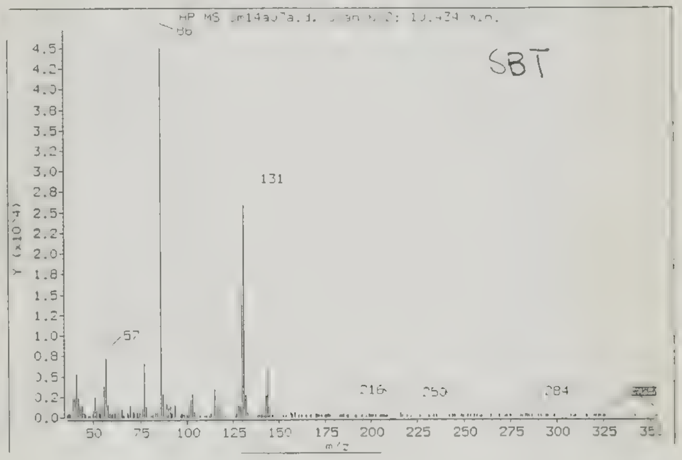
KR. 120-130° / 0.06 mm Hg.
0.12 g white oil, added waste

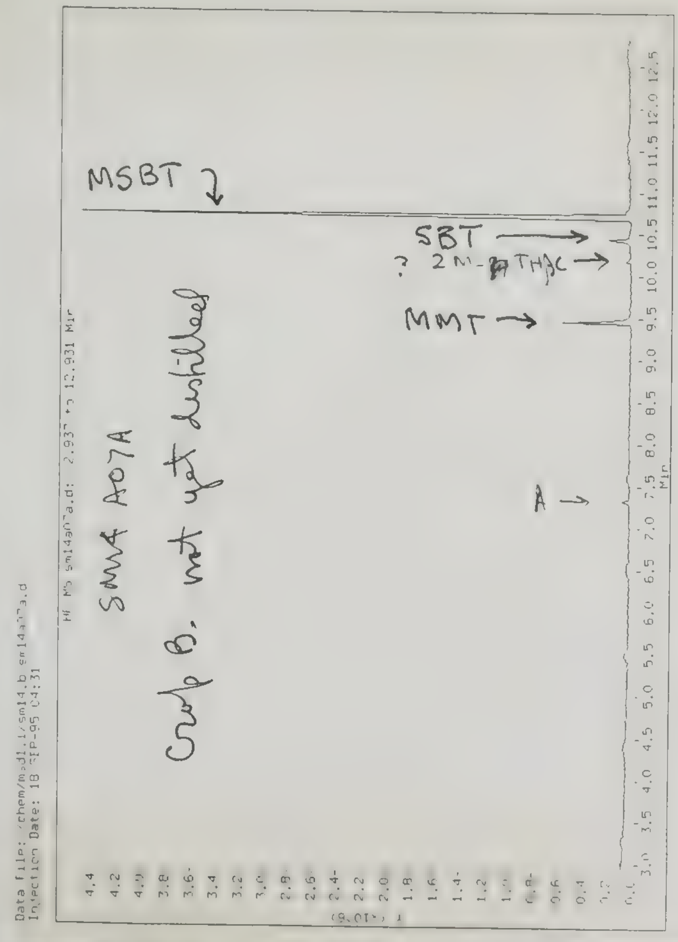


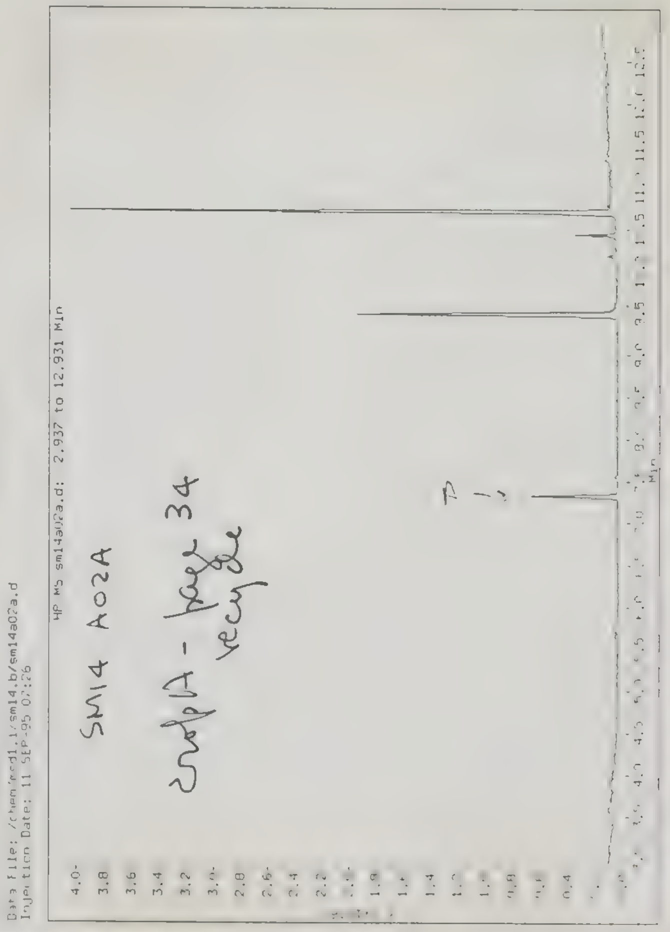

HP MS sm14a02a.d. Scan 762: 7.321 min.
A
57
91
145
205
220
305
334
352
Y (x10^5)
m/z


143
2-Me THβC ?
MW 186
N-CH3
MW 143
42
115
186
Y (x10^4)
m/z


HP MS sm14a07a.d. Scan 523: 9.456 min.
44
MMT
NMT
131
103
174
232
283
Y (x10^5)
m/z


86
SBT
131
57
216
250
284
Y (x10^4)
m/z


Data File: /chem/msd1.i/sm14.b/sm14a07a.d
HP MS sm14a07a.d: 2.937 to 12.931 Min
SM14 A07A
Crude B. not yet distilled
MSBT
SBT
? 2M-THβC
MMT
A
Min

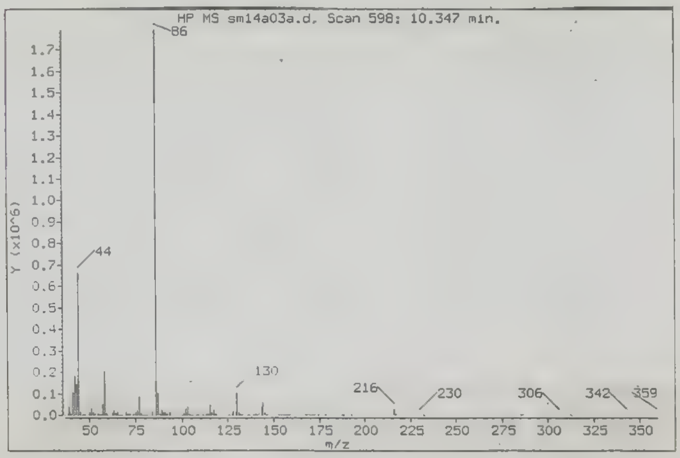

Data File: /chem/med1.i/sm14.b/sm14a02a.d
Injection Date: 11 SEP-95 07:26
HP MS sm14a02a.d: 2.937 to 12.931 Min
SM14 A02A
Crude A - page 34
recycle
A
Min

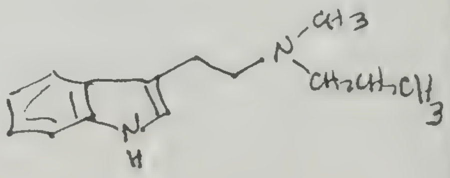
(36) repeat of SF run.

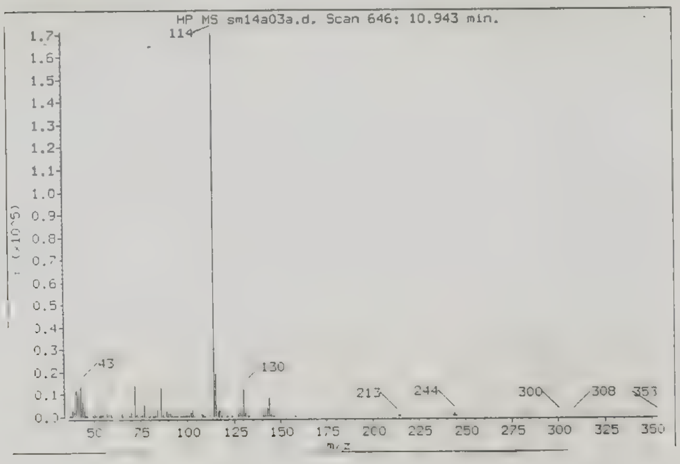
MPT

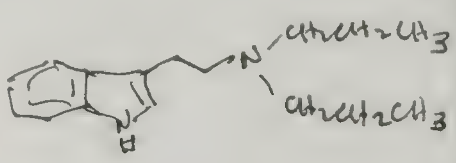
0.3 g N-methyltryptamine, into
4.5 g IPA - add
1.3 g 1-iodopropane. - reflux 1½ hrs.
strip - GCMS. more done than not
+ ~~4.5~~ ml IPA + 1.3 g 1-iodopropane - SB ([illegible]) PM. next morn
5.5 g strip - KR - 160-170°/0.05 → 0.19 g off-white oil. ff.
0.19 g

1.25°C
0.05 mm
160°
160-170°
over
0.05
0.19g









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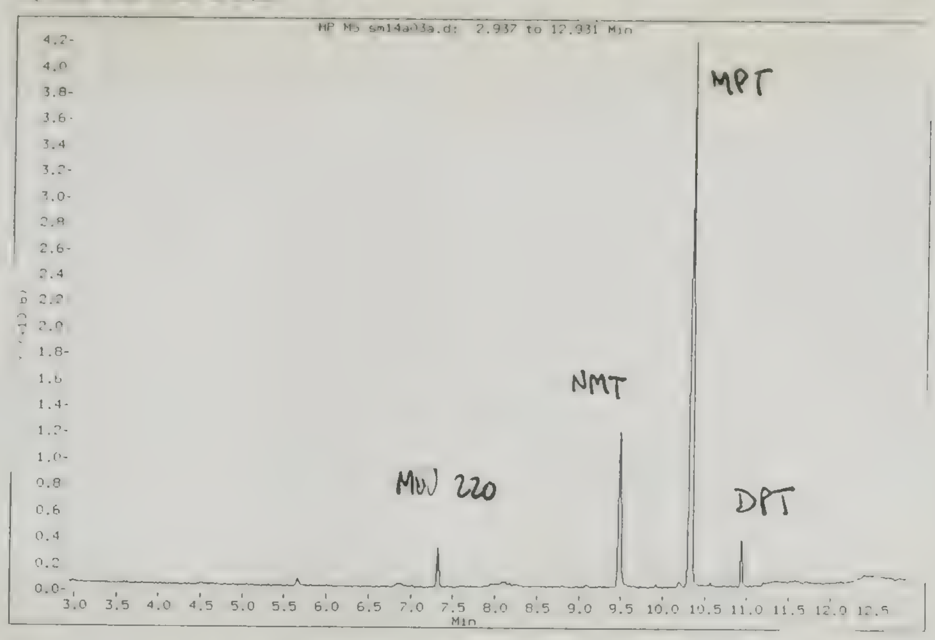
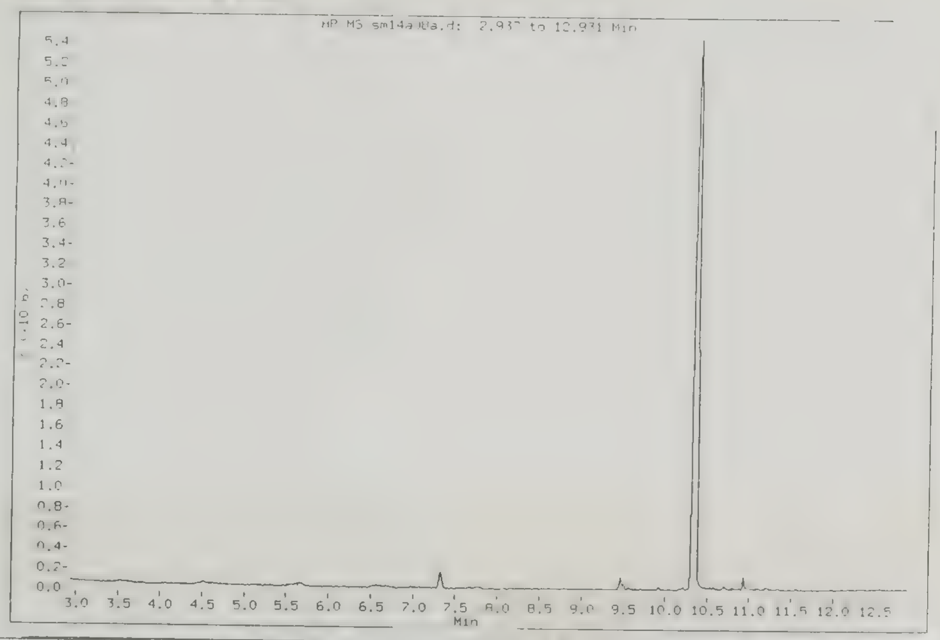
Injection Date: 11-SEP-95 07:50

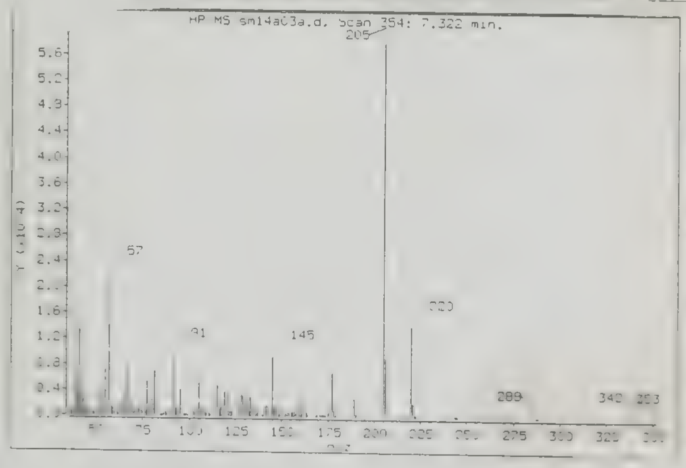


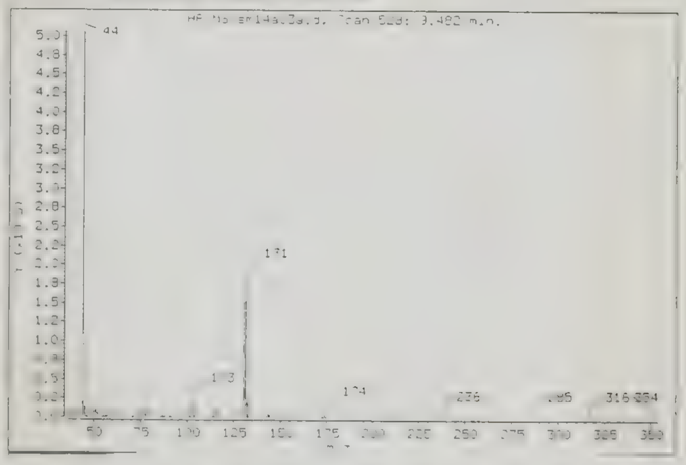
1½ hr assaw

Data File: chem msd1.i sm14.b sm14a08a.d
Injection Date: 18-SEP-95 04:50



12 more hours

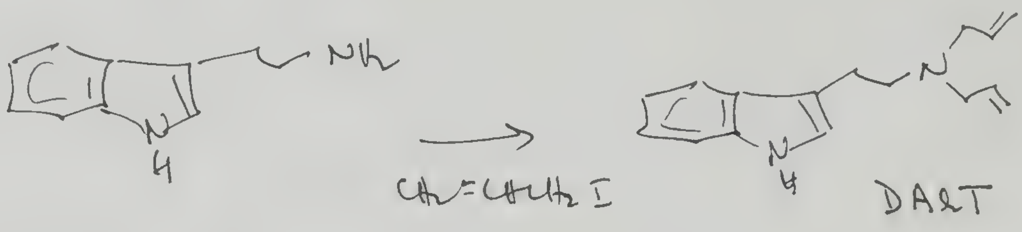




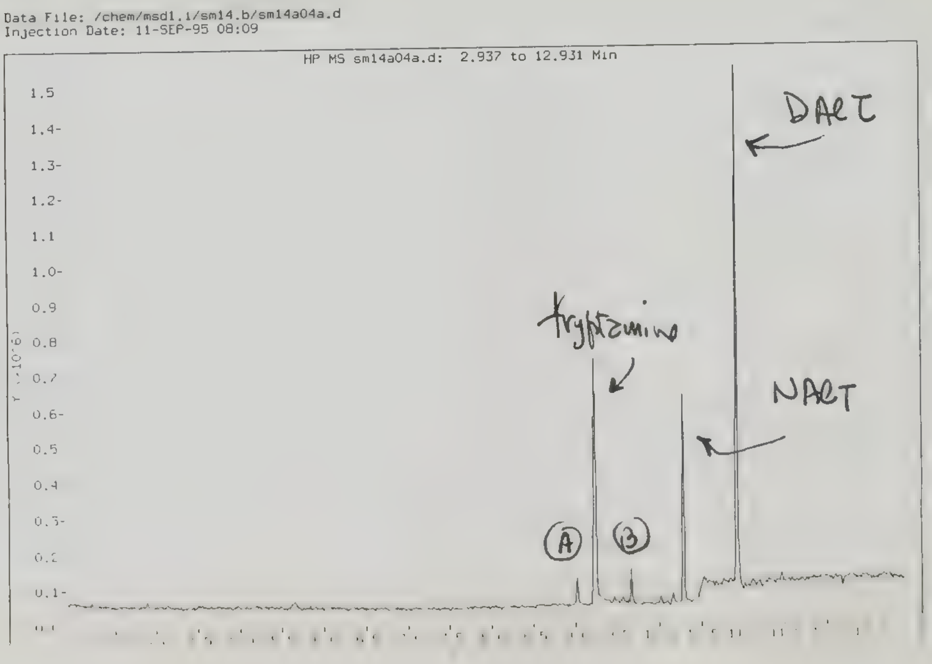
MW - 220

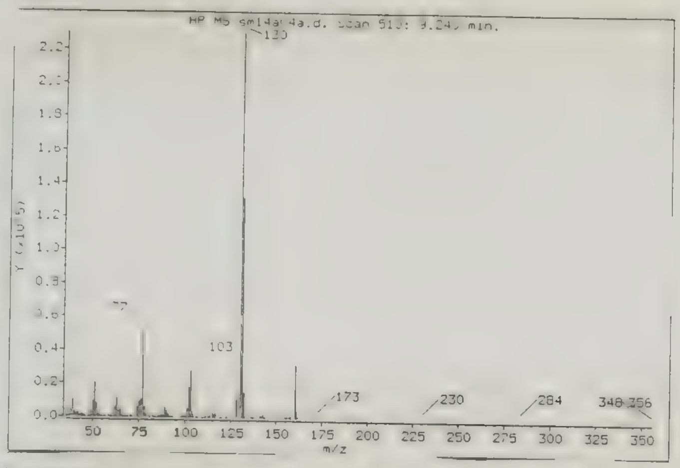
NMT

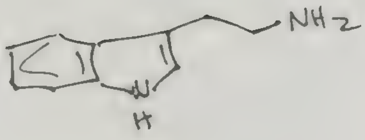
Attempt.

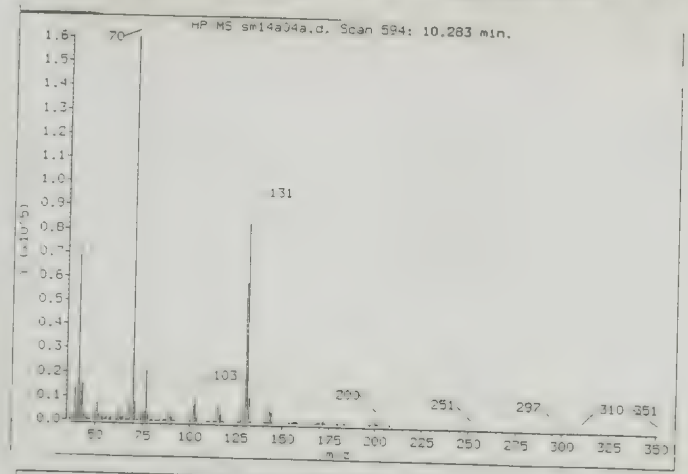


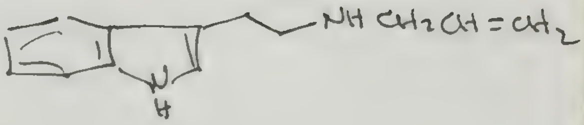
1.0 g tryptamine in
8 g IPA. add.
4 g allyl iodide - into reflux 40 minute.
Strip GCMS
+ 8 g IPA + 4 g allyl iodide - on 4^{30} PM
work up next AM - strip → no yield !!!!

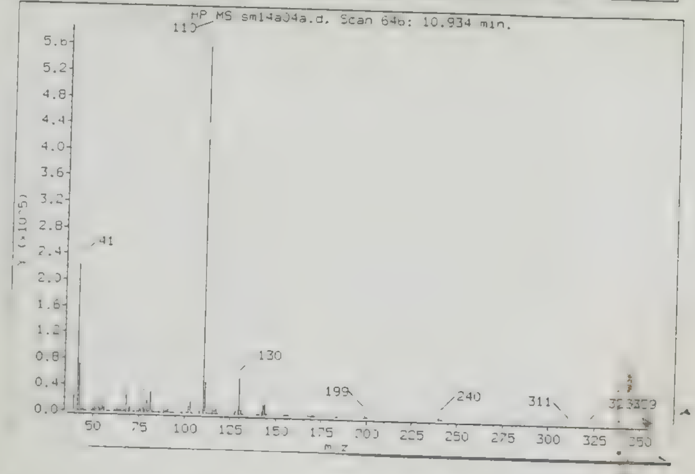


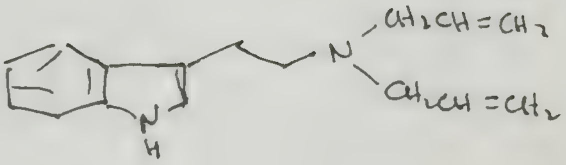

HP MS
130
103
173
230
284
348 356
m/z

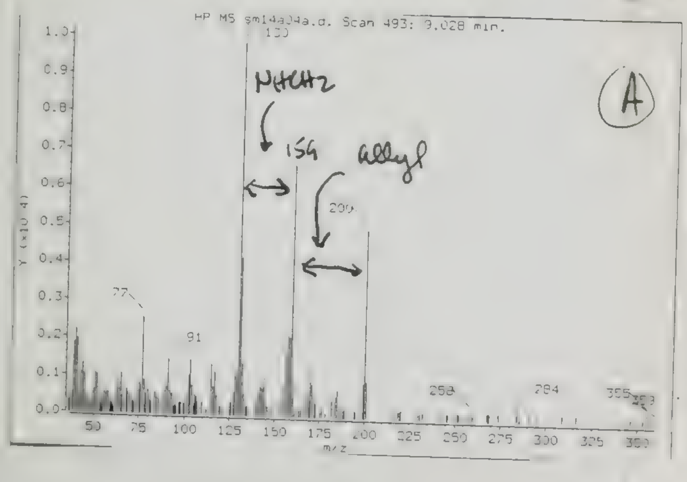

NH2

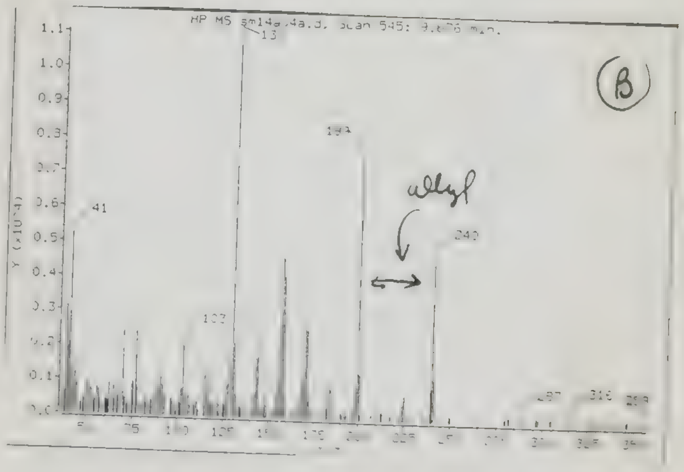

HP MS sm14a04a.d. Scan 594: 10.283 min.
70
131
103
251
297
310 351
m/z

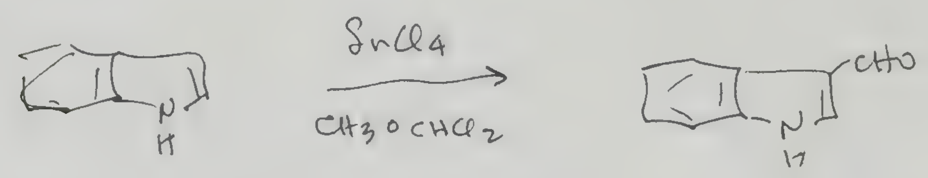

NH CH2CH=CH2


HP MS sm14a04a.d. Scan 646: 10.934 min.
110
41
130
199
240
311
m/z


N
CH2CH=CH2
CH2CH=CH2


HP MS sm14a04a.d. Scan 493: 9.028 min.
A
130
NHCH2
154
allyl
200
77
91
258
284
m/z


HP MS
B
41
allyl
240



Dry some CH_2Cl_2 by boiling 200 ml → 100 ml on SB. cover immediately.

In a 250 RB flask - mag stirrer - add
10 ml dry CH_2Cl_2 - add
1 g indole - stir → solution (under Ar) - cool to 0° c̄ external ice bath. add

12.5 ml 1 M $SnCl_4$ (in CH_2Cl_2) over ~ 2 minutes, dropwise - turns a slightly cloudy grey color. Then add:

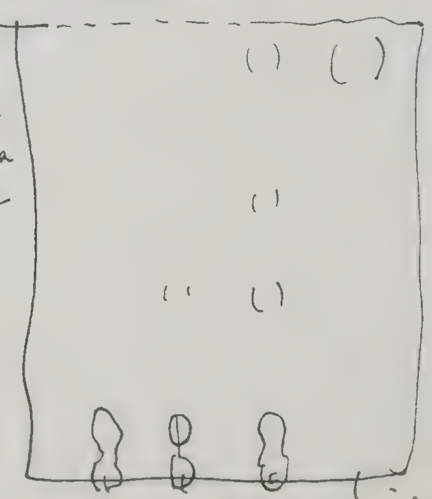
1.0 g neat Cl_2CHOCH_3 slowly (stir, still at 0°) turns a tomato color.
stir 15 min 0° - then
1 hr RT. Pour into icewater, make basic c̄ aq. NaOH → orange CH_2Cl_2 phase & colorless aq.
Separate - extract aq. c̄ 25 ml CH_2Cl_2 - combine wash c̄ ~ 1% NaOH. Separate & flash.
pale yellow phase → 1.78 g crude viscous oil.

Into ~10 ml MeOH - let stand ON → xtals down | ML up | plastic-like film on top (out)

grind up. → 0.46 brownish-cream solids

into big petri dish evap ON → wet oil & xtals wash c̄ 2 × 5 ml hexanes → indole smells
↓
brown solids 0.23g
sl. gummy solids

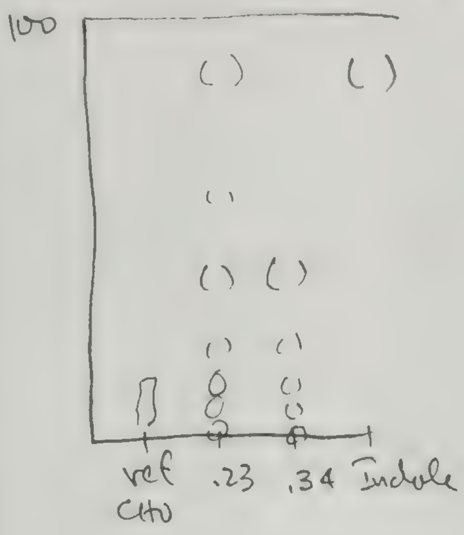
100
CH_2Cl_2
Silica
TLC



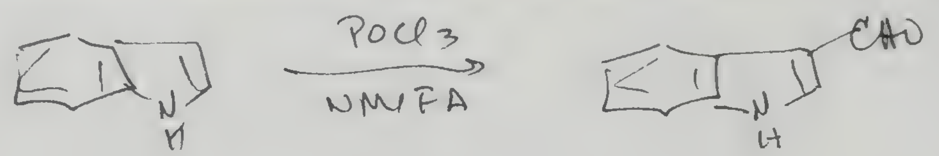
to page 41 · ref CHO .46 .23 ref indole

from page 40

combine 0.46, 0.23 g - grind under 10 ml IPA - stand ON
→ brown xtals after filtering, washing c̄ IPA. 0.34 g

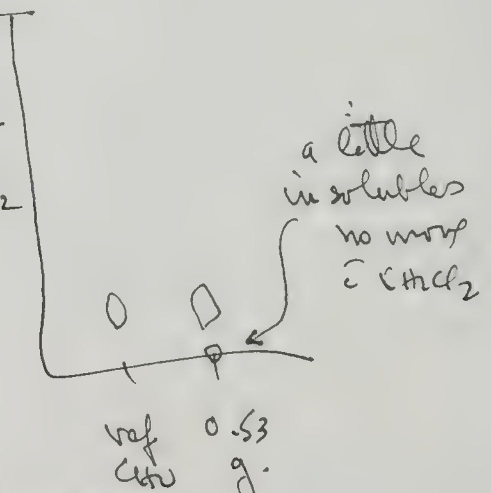


Terrible; free of indole & .5 Rf stuff -
forgot to TLC ML - red brown oil as residue

(42) Try 

|| Pihkal 580

7.2 g $POCl_3$
6.7 g NMeFA let stand RT start 1700 on docks.
by 17:35 not claret enough – onto SB.
Δ 6 minutes – now claret. ∇ to body Temp.
add:
2.5 g indole – vigorous – gets very hot – black – bubbling.
let go ~5 minutes – into 150 ml H_2O – stir ON.
AM – decant from black oil – + 10, maybe 15 ml
MeOH – scrape, scratch → solids.
filter – wash c̄ small amts MeOH
↳ 0.53 g lavender solid.

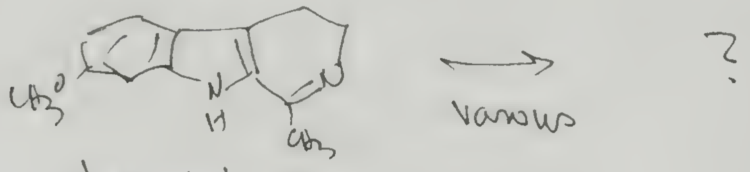
1.00
TLC
CH_2Cl_2


to page 43

Repeat, but cold.
page 42 ←

7.2 g $POCl_3$
6.7 g NMeFA. Δ SB ~ 10 min → claret. ▽ to ice bath. stir. add
~~2.5~~ 2.5 g Indole
still very exothermic, even at 0°C.
stir until all at ~0°, no more R4.
heavy black oil - add ~150 ml H_2O -
stir → water insol. oil - red color into water.
decant, + water 2x
stir until black oil + almost ~~[illegible]~~ no red into water.
decant - then + 10 ml MeOH - stands ON.

(44) trial:



harmaline H_2

A bunch of trial changes of harmaline, different conditions, to challenge its oxid, H_2 stability. H_2 here hydrogen, there harmaline

(A) H_2 in water, few drops HCl Hugh.

(B) H_2 in water, few drops 25% NaOH. Hugh.

(C) H_2 in water, c̄ Vitamin C. Hugh.

(D) H_2 just in unbuffered water. Hugh.

(E) H_2 in H_2O, c̄ strips of garden ivy - Hugh.

all - unchanged H_2 by GCMS

(F) into acidified (HCl) water, + Adams catalyst, + aq. $NaBH_4$ soln - hot - sparkles - make basic, xtrt c̄ 90/10 Toluene BuOH. GCMS. entirely tetrahydro harmine Ha.

46

24.58 g nicotine (just over .15 mole)
use ~~2~~ .3 mole HI (to ph ~ 2)
at 50% strength.

into 200 mL denatured
add 75 mL 50% HI (try to get pH c̄ paper
failed as ~~a~~ the paper should have been
water-wet first - I forgot. here it is
strongly acid.
play c̄ ether, → 2 phases - no xtals - play - dilute is better xtals?

dilute to 1 L. c̄ denatured EtOH - ether to seed,
add total 1 L. ether → xtals - stand a ~~white~~ white -
(a bit at a time, c̄ stirring)
filter, wash c̄ 50% ether/alcohol.
↳ light yellow xtals
air dry ON → 38.50 g

ML's + ether again → 2:1 ether/EtOH ratio -
more light yellow xtals
filter, wash c̄ 2:1, air dry ON
↳ 14.0 g

ML's of ML's - turning very dark
OUT.

Σ 52.50 ~~g~~ yield - 63%

Continue from (46)

52.50 g di HI salt of nicotine - completely dry. dissolve in 150 mL MeOH (not sol at all in IPA!) add 20.34 g nicotine (converts to mono-HI) add 39 g CH_3I (10% xs) - onto SB reflux at 4:45 PM.

slight darkening in evening - let go ON -

off noon. play a bit, scratch, ether, => seed.

Pour all into a beaker while still very hot - seed takes - all sets of xtalline solid. stand ON. break up and filter, wash c̄ ~4 20 mL portions of MeOH - Air-dry to constant wt. 98.24 g pale yellow xtals

>100% Y?

98.24

MW's

nicotine	162
N·HI	290
$N\cdot(HI)_2$	418
CH_3I	142
$N\cdot CH_3I$	304
$N\cdot CH_3I\cdot HI$	432

72.84 g → N·HI

Peganum harmala → alkaloids

1.5 g P. harmala seeds - grind to powder in mortar - [illegible]

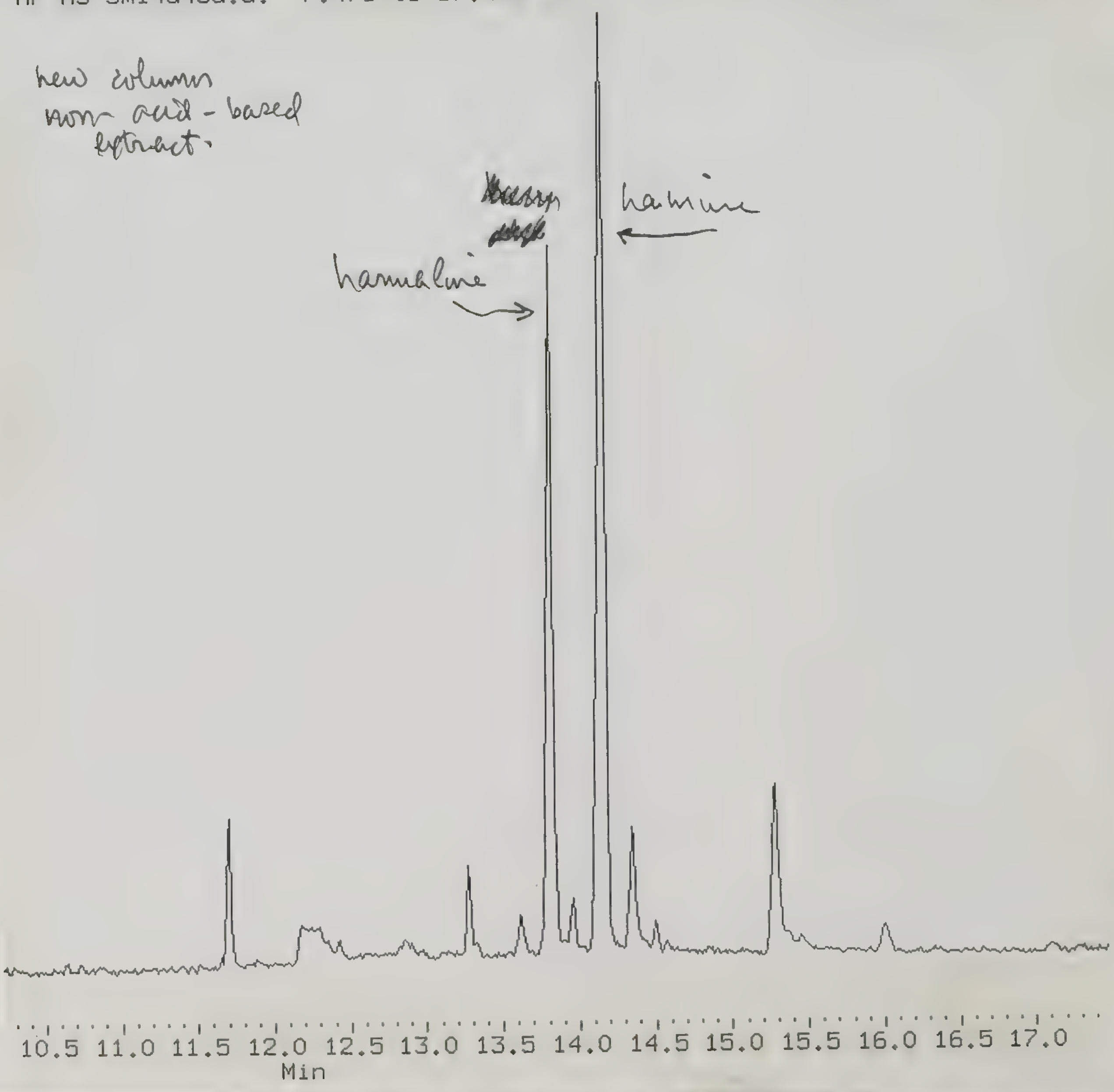
5 mL sat $NaHCO_3$ +

5 mL CH_2Cl_2 - boil for 10 minutes
add CH_2Cl_2 as needed.

decant - wash solids c̄ CH_2Cl_2 → dry → flash
→ 0.11 g plant-smelling oil!

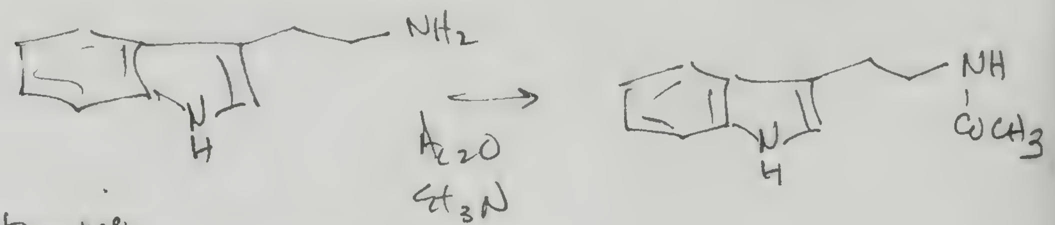
dissolve in 2×2 mL CH_2Cl_2 - flash → 0.055 g - plant oil

HP MS sm14a45a.d: 7.473 to 17.467 Min



51

(52) Attempt:



16.0 g ~~[illegible]~~ tryptamine (MW 160) 0.1M – add.

25 g Et_3N (MW 101) 0.25M – >100% xs., add squirtwise good stirring

11.2 g Ac_2O (10% xs). very vig – gets hot – stir until exotherm done – onto SB ON

AM – 2 phases on SB. strip down to a thick, gooey sludge – stand a few days – add ~50 ml CH_2Cl_2 – very slow to go into solution – then clear solution – add more CH_2Cl_2 – add 100 ml H_2O, HCl → pH acid.

Separate – extract aq. c̄ 2×50 ml more CH_2Cl_2 – wash CH_2Cl_2 phase 1× w 1/4 sat $NaHCO_3$ – very blue pH paper – separate – strip → 12.57 g dark viscous oil – to KR. Vac slowly from 0.5 – 0.4 – 0.2 – 0.1 mm. distil.

185–200°/0.1 mm/Hg. about 9/10 over – residue looks unfriendly stuff. Oil is viscous amber. looks good.

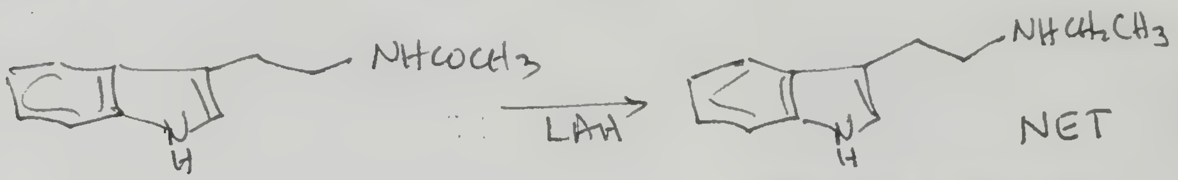
→ 9.45 very vis. oil – amber.

13.30 tare.
22.67
9.37

flame out → 9.37. external play → white xtals
glass
no – is fused solid.
– MeOH too sol, hexane → solids
IPA → xtals.
CCl_4 → nice xtals

mp 70–73
mp 71–7
73–74

54 attempt:



mono ethyl tryptamine
what do I call it?
MET is N-Me-N-Et T
ET is α-ethyltryptamine
N-ET ?, no: NET

|| page 22

A solution of the hard glass acetamide, page 52, in 30 ml dry THF. under Ar. Heating → pale yellow solution (wanted 2.02, used 2.31 g - terrible glass).

A solution of LAH in THF (1 M) 60 mL - brought up to almost reflux, under Ar, stirring, 3 N RB 500 ml.

Add amide dropwise - good stirring. Hold at reflux 10 PM.

Stir ON - sample at ~10 AM - (let cool, but stir) done

Next day - add 50 % aq-THF c̄ stirring (total 20 ml) filter through paper - wash c̄ 3×25 ml OK THF. ML base to wet pH paper - strip → 1.60 g pale cream-colored oil.

KR. 128-135°/0.1 mm Hg → white oil that xtallizes in the receiver.

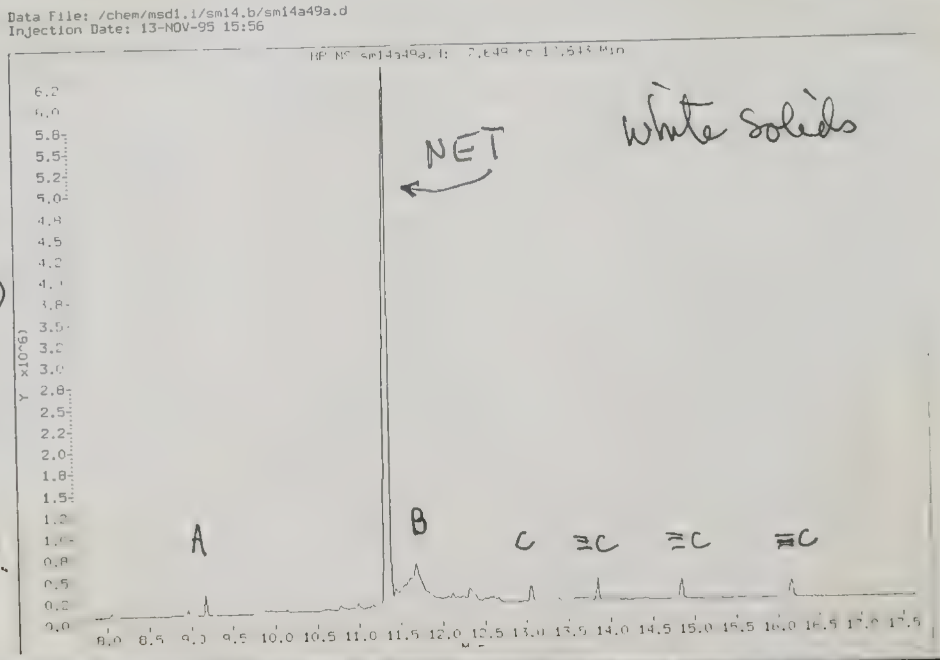
↳ 1.58 g - pushed too far - xtals c̄ drops

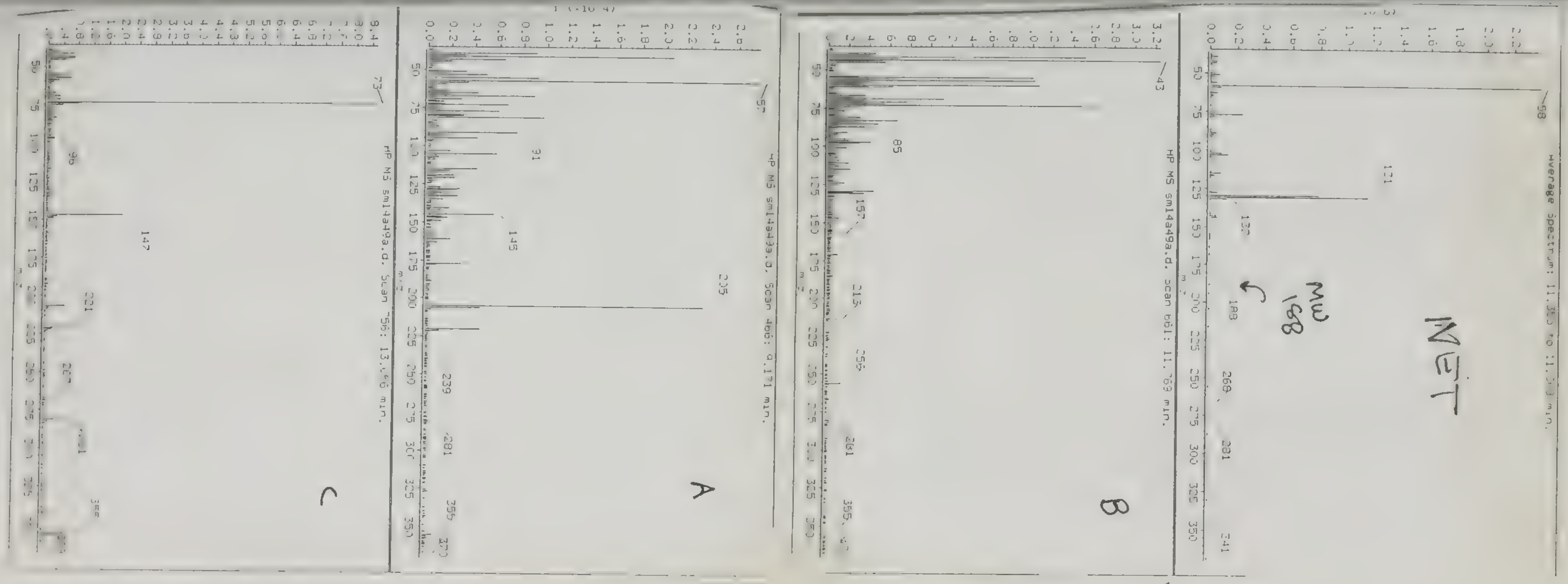
1.60 g stripped

0.1 mm
90° no
125° 0.1 start white,
little more by 140° off.

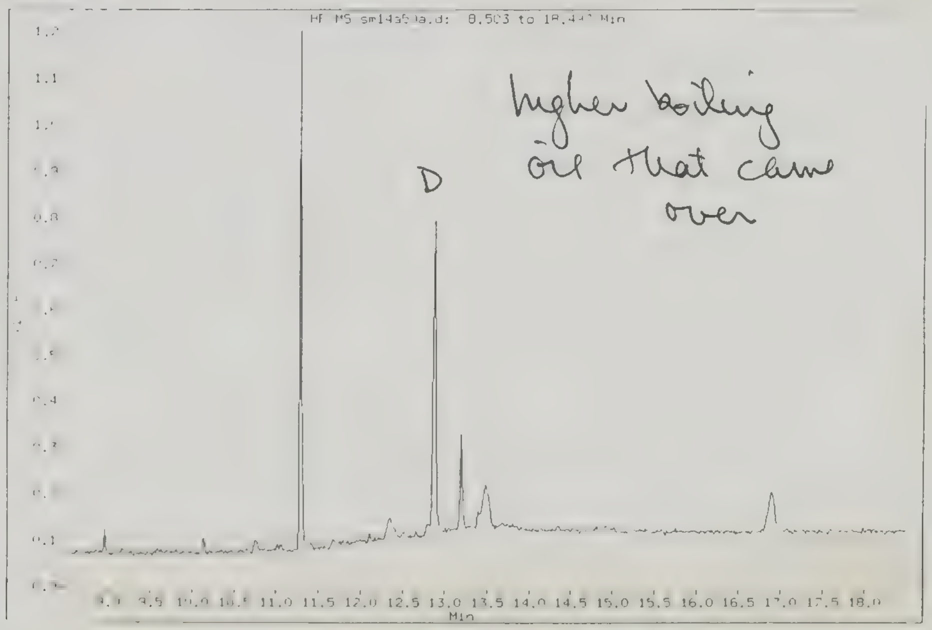
free base white xtal (turns brown c̄ time)
as white, mp 80-81°

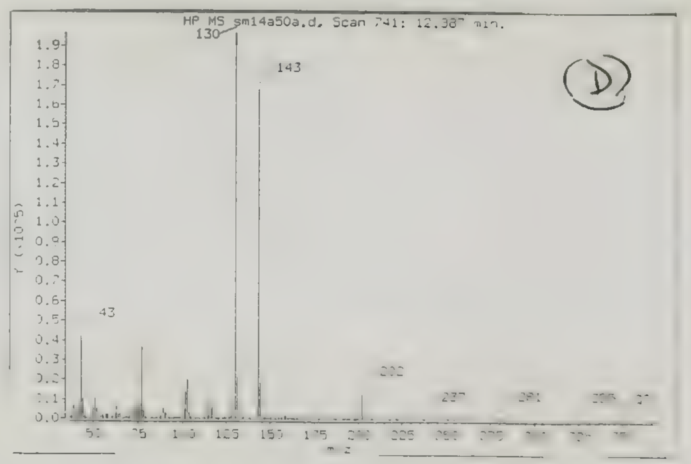
150 mg into 750 mg IPA
6 drops HCl
9 drops ether →
sl cloudy - then xtals!
104 mg
mp 181-182°

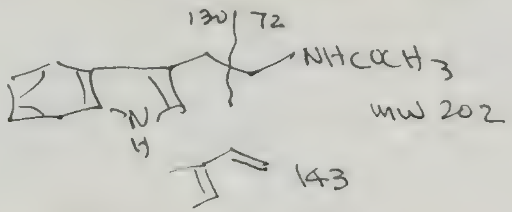




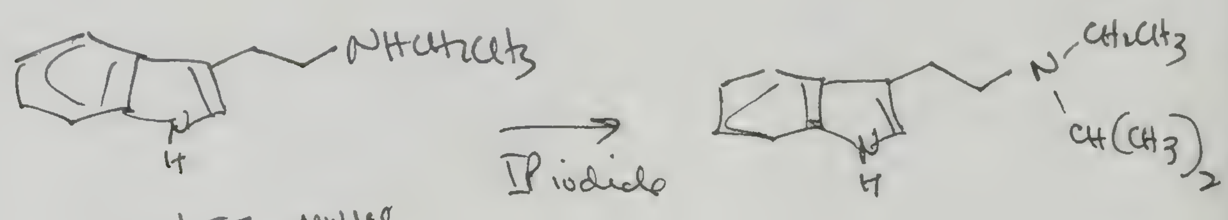
Data File: chem/msd1.i/sm14.b/sm14a50a.d
Injection Date: 13 NOV-95 16:30







(56) Attempt:



NET MW188

EIPT

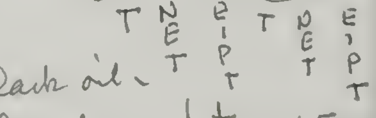
|| page 32

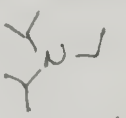
0.33 g freshly distilled (white xtals) NET, into
4.5 mL IPA - add
1.3 g isopropyl iodide
onto reflux SB ~6PM - in
AM ~ 10 AM - add
2.0 g isopropyliodide. back on reflux.
off 10 PM. 28 hrs.

strip - to dark resin

Add to 100 mL aqueous, pH red ?! make strongly basic c 25% NaOH - pH blue - xtrt 2x 25 mL CH2Cl2 - combine - wash c H2O - flash on RE. 0.31 g of dark oily residue - GCMS before KR.

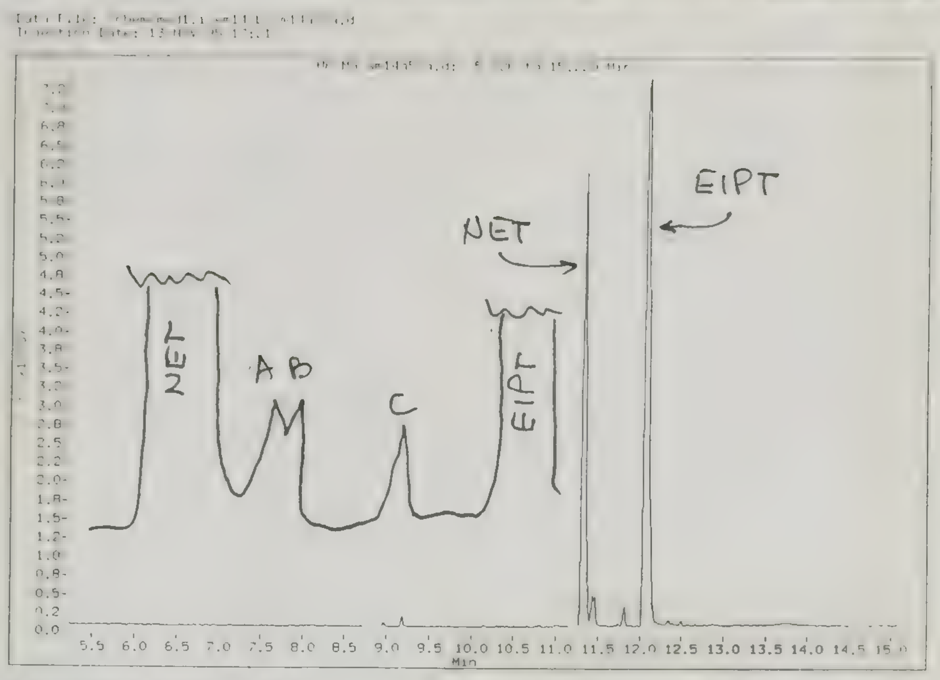
0.31 g   2/3 done - TLC for reference purposes. ⟶
try to finish up c a little bit of base.

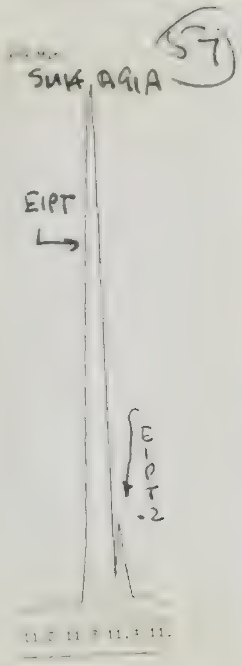


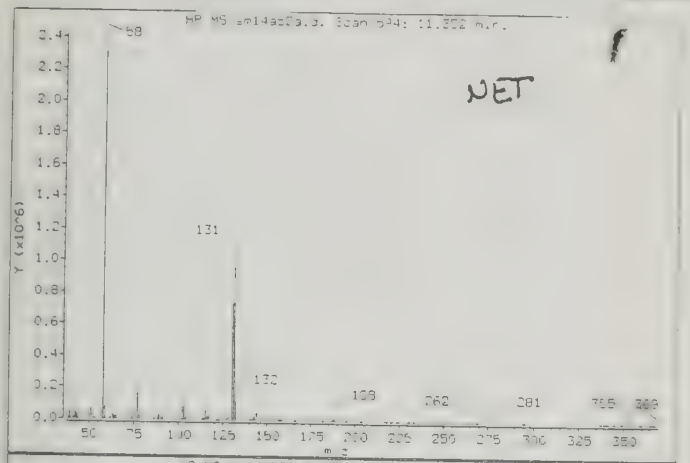
All of .31 g crude EIPT
4 mL IPA
1.3 g Isopropyl iodide
0.25 g    onto SB. 2:20 PM
at 3:10 - no change - ON
total 36 more hours - strip → black oil.

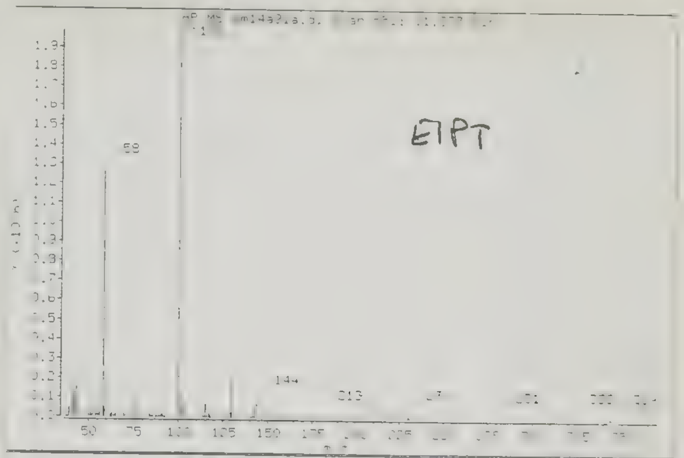
into water - CH2Cl2 → white/black. + 15% NaOH → cloudy - xtrt 2 x 50 mL CH2Cl2 - flash → black oil onto KR ~0.1 mm   0.13 mm. 80° no

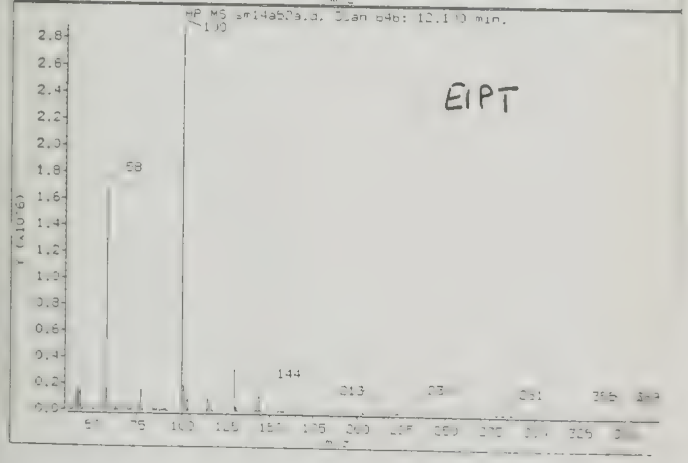
0.13 mm 80° no
130° no (0.11 mm)
over 150-160° cleanly, amber, 0.1 mm.   0.24 g

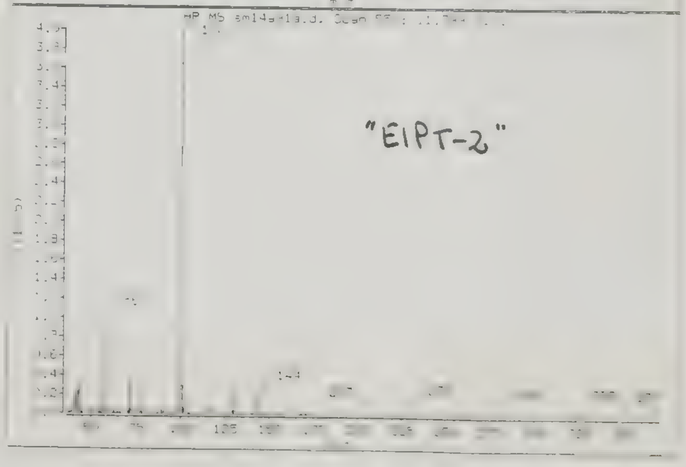












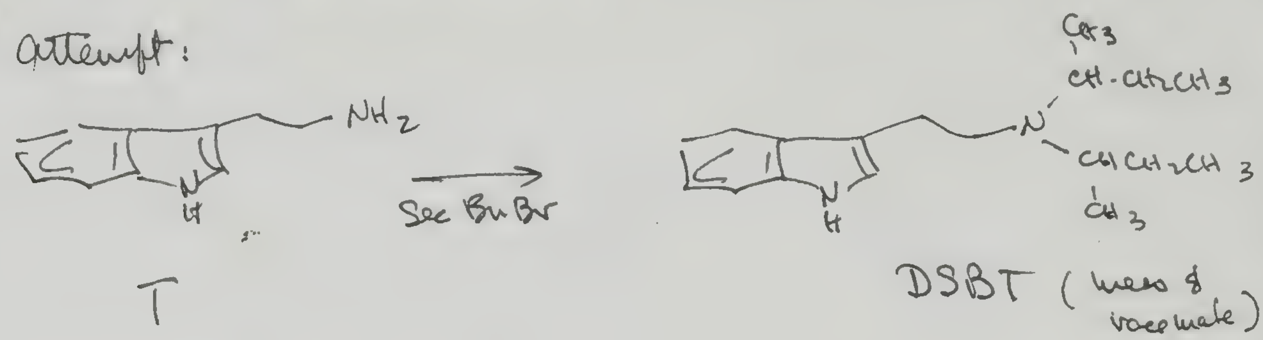
(A) 72 130(131) 202 $\{CH_2N$ (C_3)

(B) 72 (130)131 202 $\{CH_2N$ (C_3)

(C) 44 86 130 small 216 ext. small $\{CH_2N$ (C_4)

(neutral) displacement of alk gps c̄ I⁻ ?

(58) attempt:

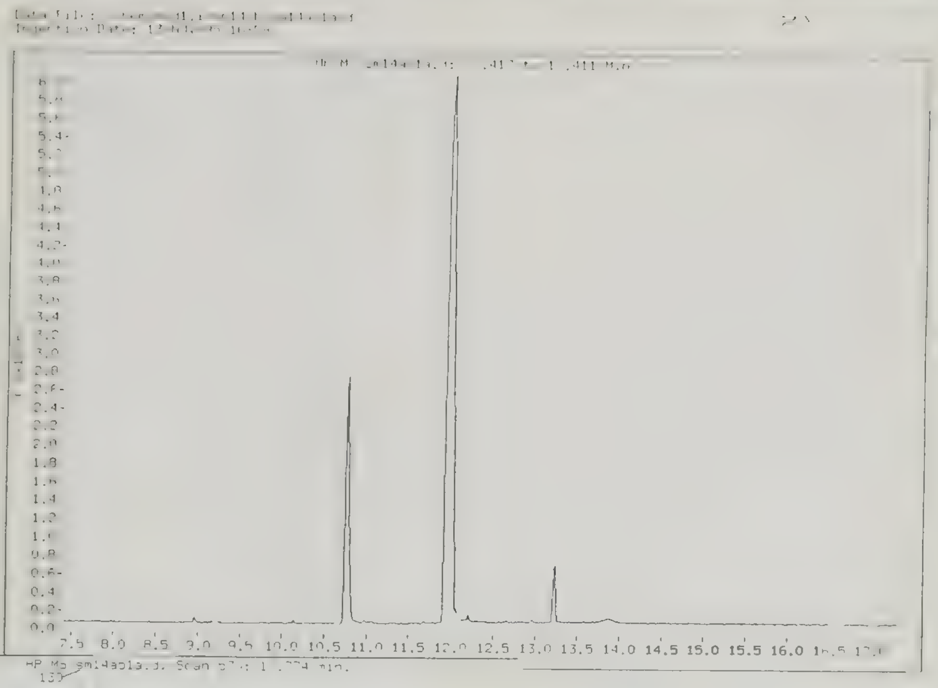


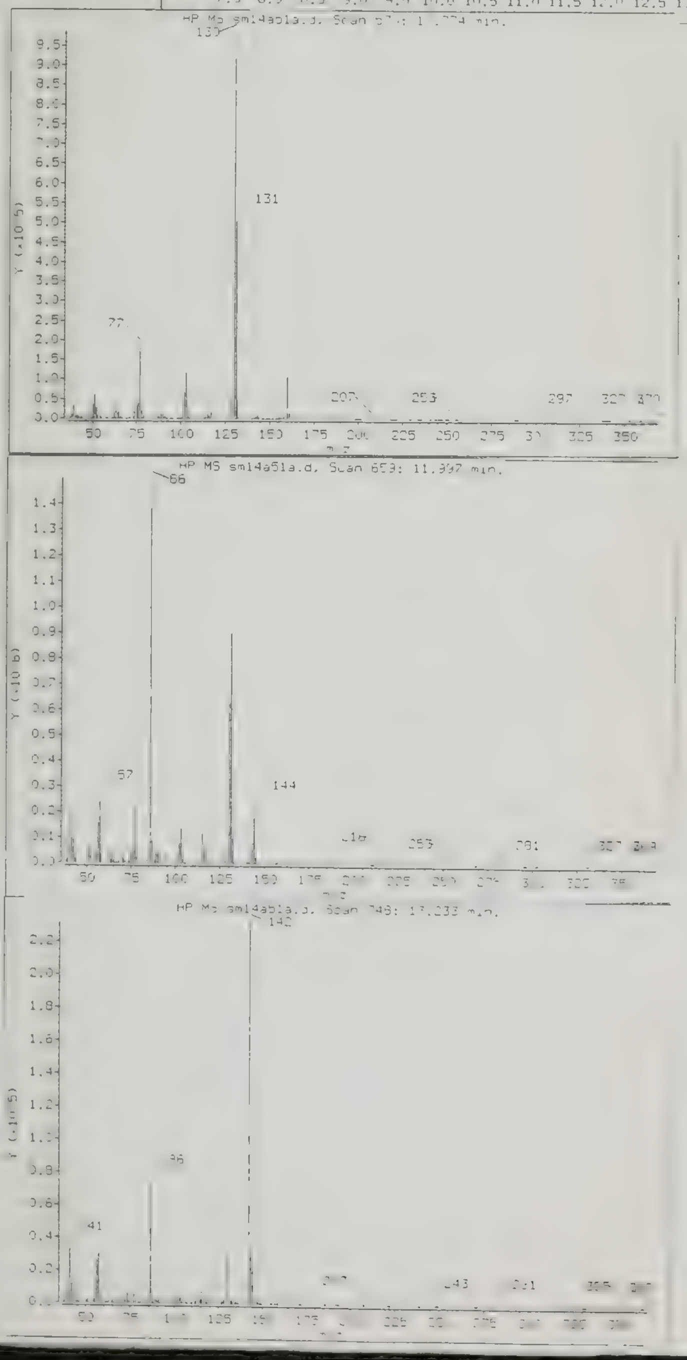
1.0 g tryptamine, into
8 g IPA. - warm, no, boil to give solution. slow, not low; add
5.5 g 2-Bromobutane - onto reflux SB - 18 hrs total
into 150 mL H_2O, add 15% NaOH → blue color & cloudy - xtrt 2x50 mL CH_2Cl_2 - back-wash c̄ H_2O
flash → 1.72 g dark residue - to KR.

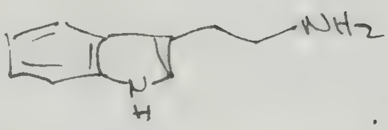
Starts over ~120°/0.05 mm - very first, amber, then colorless.
end ~150° ⟶ 1.17 g white oil.
drained, c̄ heat 1.14 g
in a week or so - two globs of beautiful white xtals

Small amt, c̄ IPA, c̄ HCl conc, c̄ Ether → fine white xtals
mp 166-
SEA 170°!

All into 6 mL IPA - clear soln. add conc HCl (21 too little, 25 drops too much)
Add ether to turb (14 mL) stir → xtals. stand 1 hr -
filter, wash c̄ ether
→ 1.27 damp, 1.07 dry white xtals.

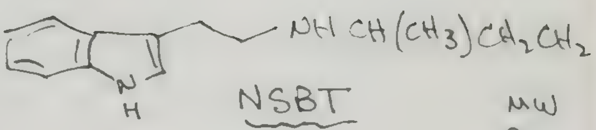






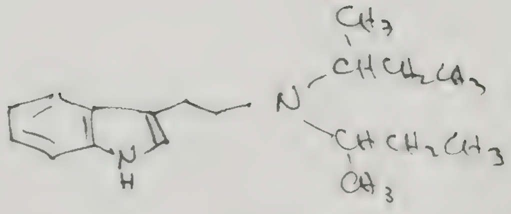
MW
160

Tryptamine
I



NSBT

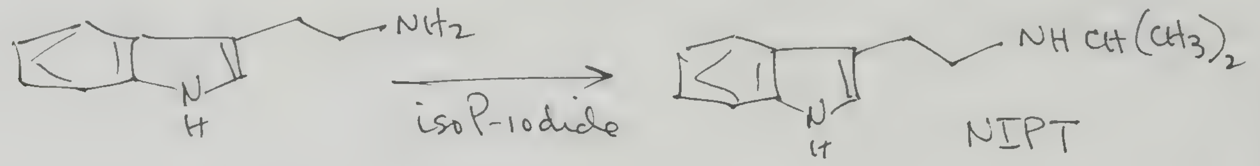
MW
216



DSBT

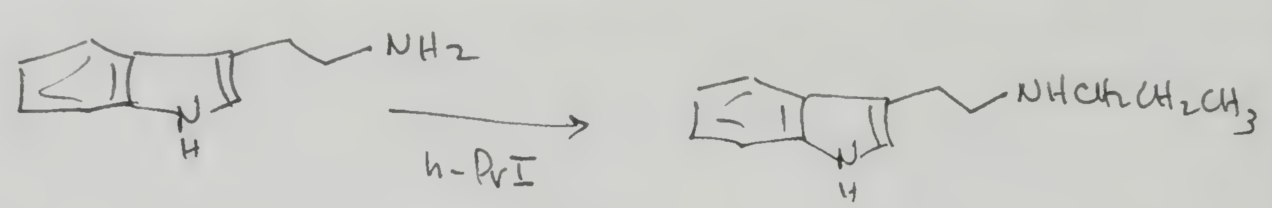
MW
272

(60)



3.2 g tryptamine (20mM) into
25g IPA   add
6.8 g isopropyliodide (40mM) - onto reflux 5^00 PM.
in mantle, under reflux. 36 hrs.
off - Strip → dark oil. iPrI slow off. dark residue -
play c̄ seed - no -
Into H2O, CH2Cl2 + 15% NaOH (pH → acid to base). ext 2 × 50 ml
CH2Cl2 - separate. ~~[illegible]~~ → separate again - org ↓ -
slow, careful. not a good separation : lotsa CH2Cl2 - separate
flsm → dark oil. - lose some due ~~to~~ water.
2.19 g dark oil - NIPT crude xtalized on
distill at KR. 0.05 mm OK before. 0.2 mm during.
80° no   0.08 + ag Hg(??) . want the open pentafore
white oil over at 130° - distil 130-150°
1.51g   total weight 1.51 g - drain out c̄ torch → 1.30 g - xtals = forming
120-150°   dissolve in 6 ml IPA
130-150°   HCl → blue/red ~~[illegible]~~ 30-34 drops.
xtals form 1/2 way through. add
4   another 4 ml IPA - Σ 10 ml
+ 20 ml ether → stirrable mush -
filter - wash c̄ ether (~ → curds, now). air dry.
↳ 1.58 g · HCl mp 224-227°

(small amt - ext. IPA - flats mp 94-95°)



11 p60

pass #1 — 3.2 g tryptamine (2 mM) into 25 g IPA - add 6.8 g (4 mM) n-Pr.I. onto reflux - off 48 hrs. strip on RE.

dissolve in CH_2Cl_2, add H_2O, add 5% NaOH → immediate white cloudy - separate, wash aq c̄ CH_2Cl_2 combine, wash c̄ H_2O, strip. There is residue on all flasks, funnels etc, not sol H_2O or CH_2Cl_2, but acetone cleans everything. Quat?

↳ 3.56 g v. dark oil (A) 10% T, 50% NPT, 40% DPT

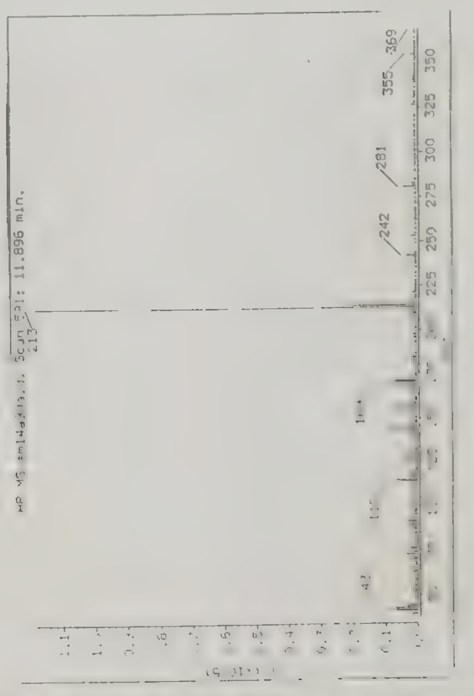
pass #2 — 25 g IPA. 6.8 g nPrI. reflux SB ~ 1½ days - off - strip → dark oil ~~0.1 mm Hg~~ into ~ 50 ml CH_2Cl_2 + 100 ml H_2O, 5% NaOH → white cloudy in aq. separate - xtrt aq c̄ 2 x 50 CH_2Cl_2 - combine wash c̄ 100 ml dilute NaOH - flash → 3.27 g black oil (B) 20% NPT, 80% DPT

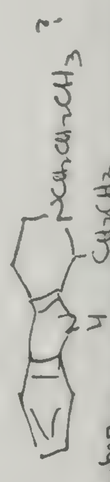
Forget mono. go for di.

pass #3 — into 25 g IPA 6.8 g nPrI - onto SB. ~2 AM - off 11 AM. small sample H_2O, base, xtrt c̄ 90/10 → (C) totally done.

KR the 0.53 g black oil comes over as a dark oil, distillate 0.47 g - redistill after flaming out -
120-30° / 0.05 mm Hg

62D. 0.37 g gold oil. (62D)

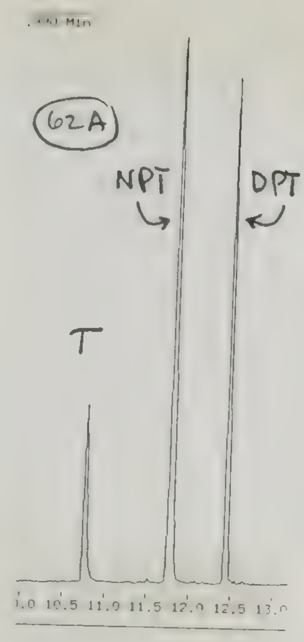


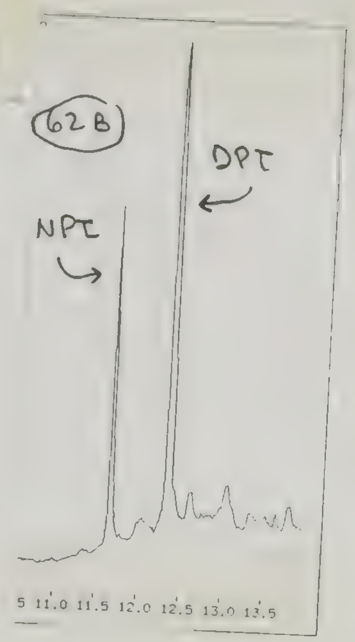


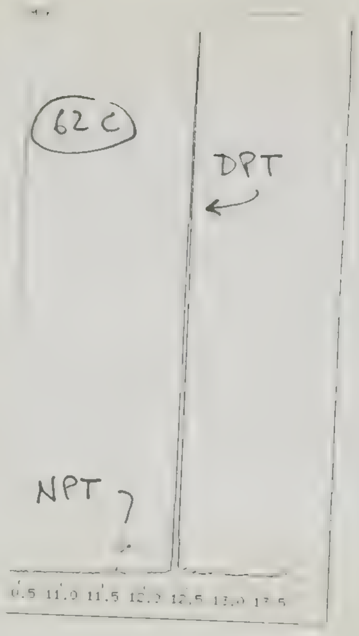
242 MW
− 29
213

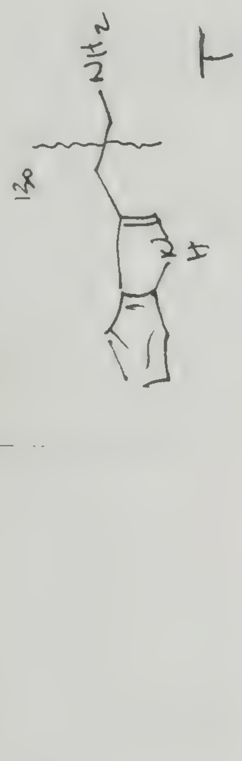
remember IPA

SM14 Δ 90A

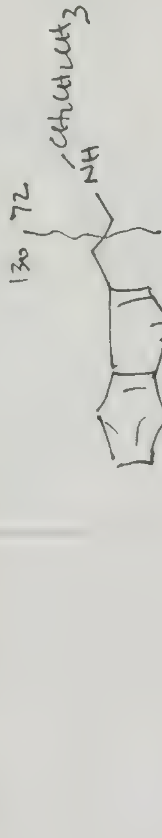




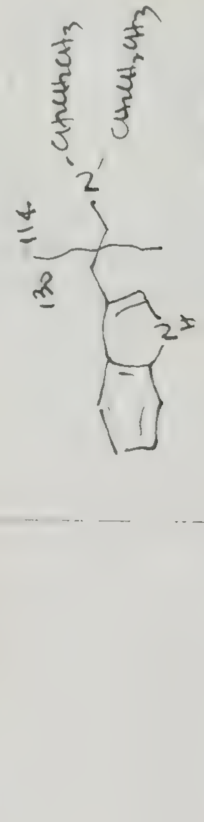




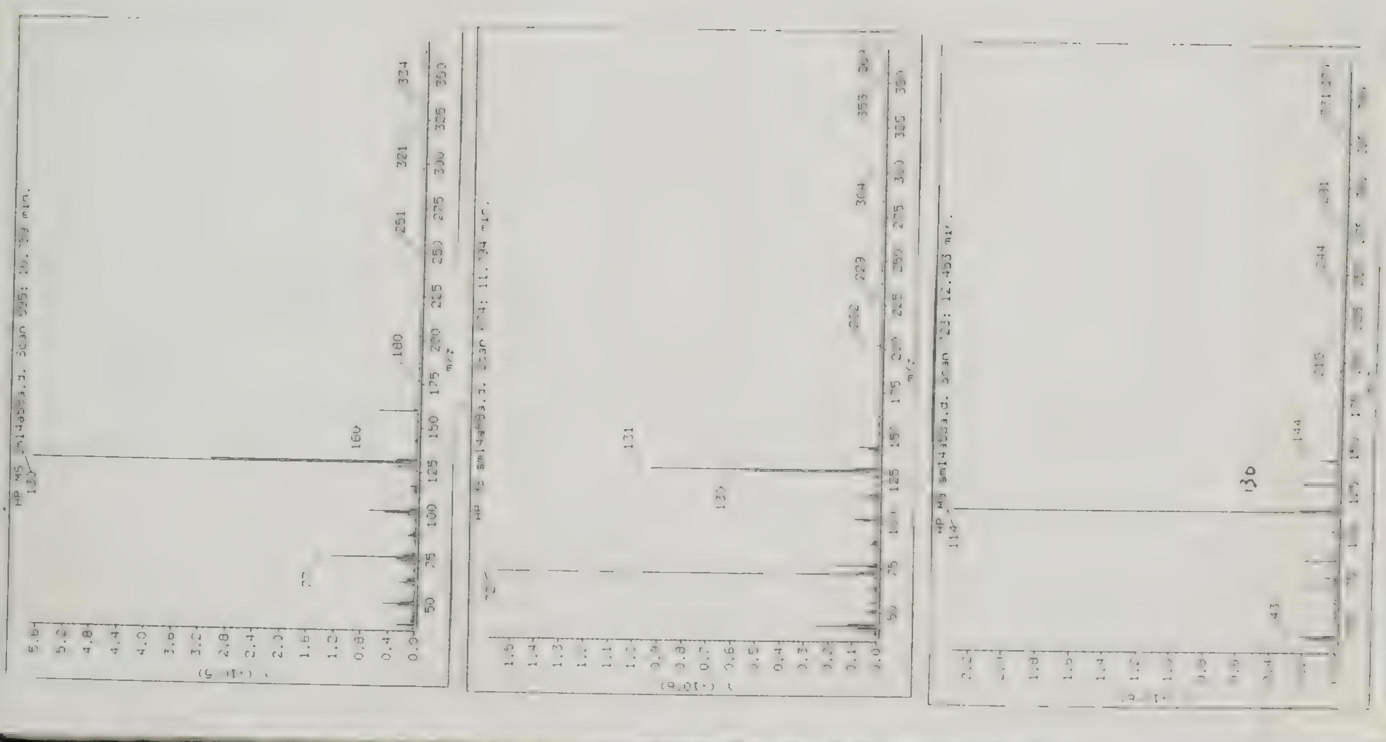
T

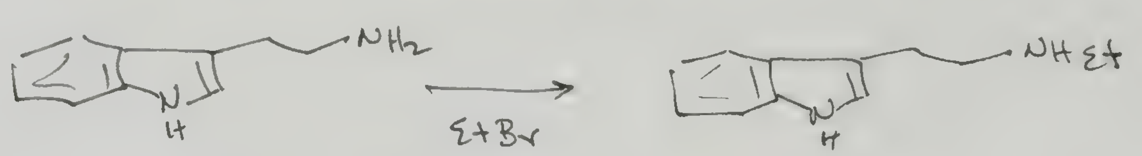


NPT



DPT





3.2g tryptamine (2mM) into
25 ~~ml~~ g IPA - add
8.72 g EtBr. onto gentle reflux c̄ stirring 8PM Friday.

---

repeat c̄ K_2CO_3 -

2.0 g tryptamine
5.6 g EtBr
15 g MeOH
8.5 g anh, K_2CO_3 } stir RT 2:45

5 hrs - off stir' filter through paper - flash well → 3.42 g

3.12 dissolve in 4×25 ml CH_2Cl_2 - rub - convert to black soln c̄ almost white solids
→ 0.55 black oil - (hydro) (cofor pot)
1.67 ↳ filter through pelite. flash → 1.67 g dark oil.
clear ↑
bumped - lost a bit.

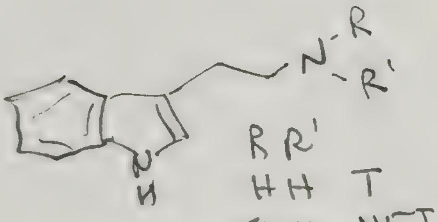
0.06 mm
0.05 mm KR. 0.08 mm 180-190°
180-190° ↳ 1.15 g white oil (A)

dissolve in 5 ml Ac_2O - Δ briefly on SB. (microscale 37° GCMS (B)) 4 hrs

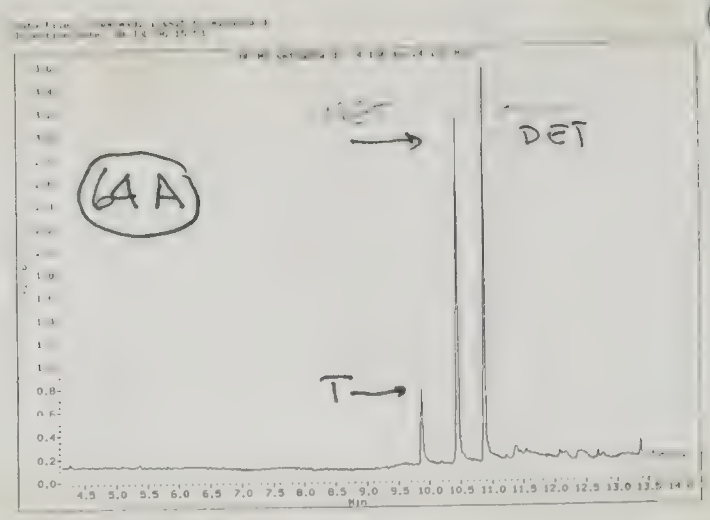
acid-base (into 0.5N H_2SO_4 - wash 2× CH_2Cl_2)
.31 crude (base c̄ 6N NaOH) - xtract. flash → 0.31 g crude

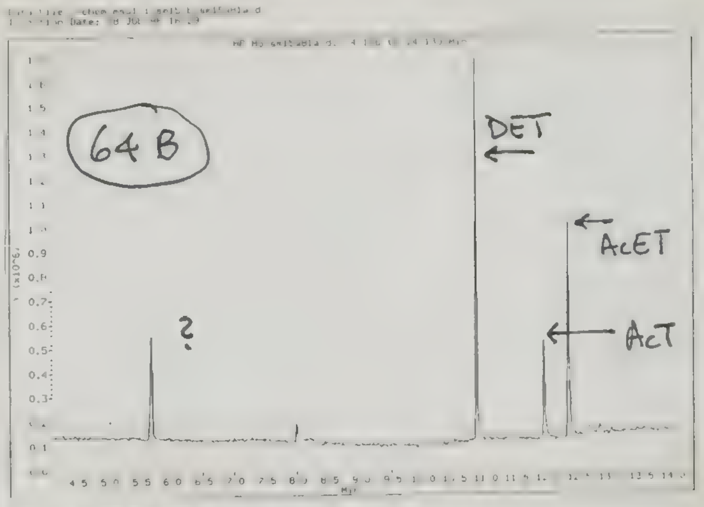
130° 0.08 KR - 155-160° / 0.05 mm → .19 g oil → white xtals
Δ → white xtals 0.175 g removed (I:64)

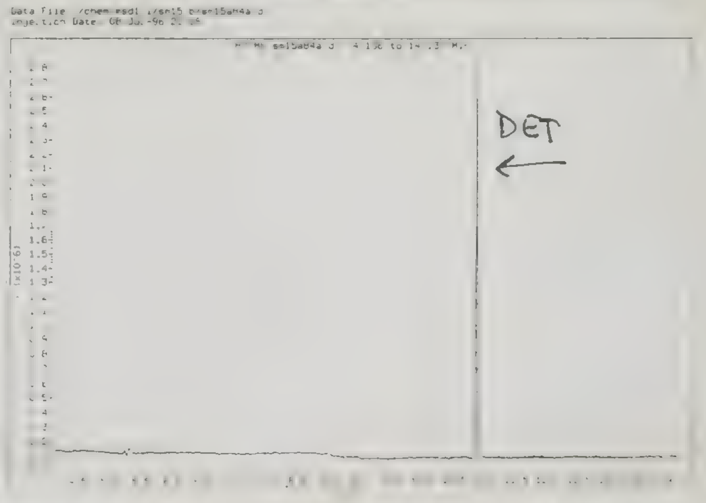
155-160
0.05!
.19

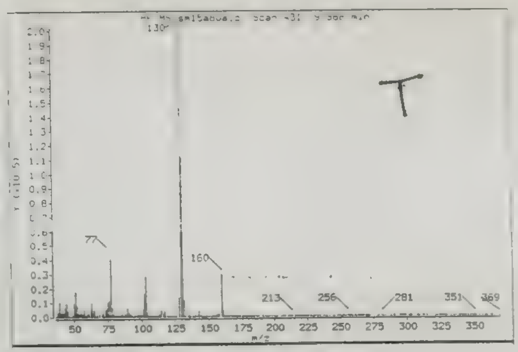


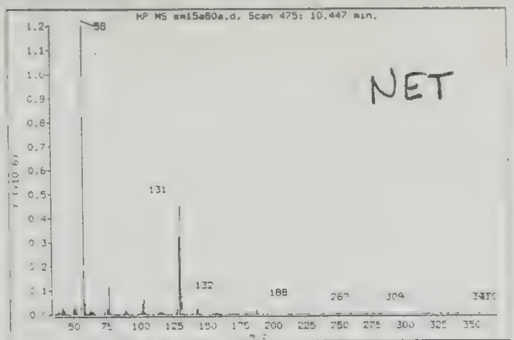
R R'	
H H	T
Et H	NET
Et Et	DET
H Ac	AcT
Et Ac	AcET





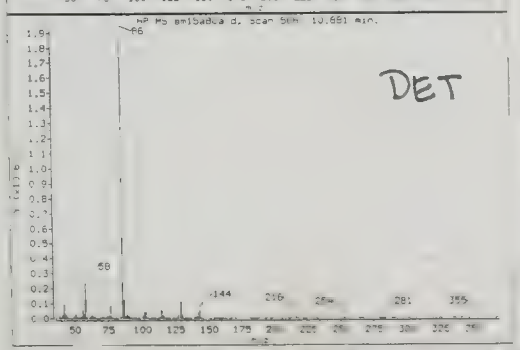


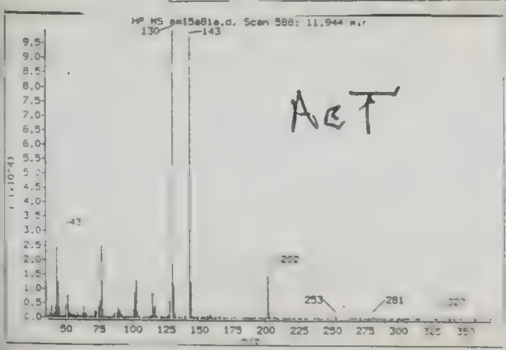


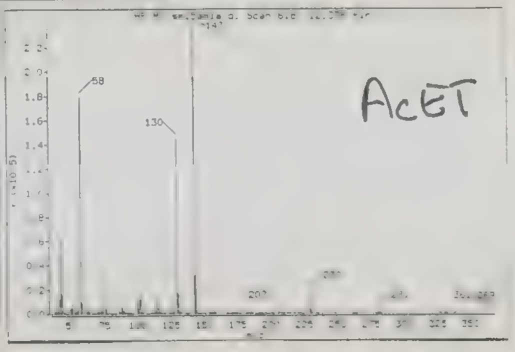


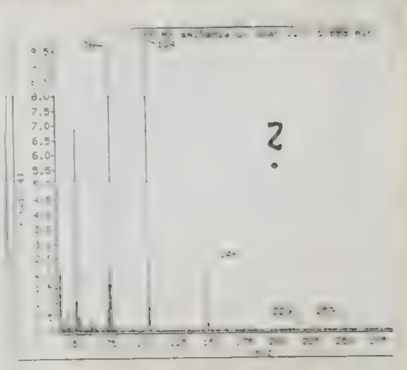
Confirm great

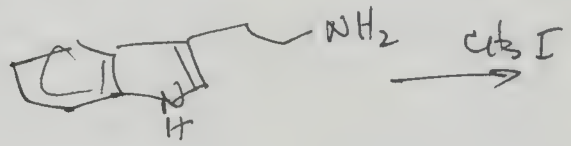
Ho Sol!











1 g tryptamine.
10 g $(CH_3)_2CO$
3 g CH_3I
stir 18 hrs.
white solids under acetone

10 g tryptamine,
40 g warm acetone (sol)
36 g CH_3I.
exotherm – add
15 g $(CH_3)_2CO$ – is OK.
stir ~12 hrs. Solids in a minute.

combine.
filter. wash c̄ acetone → cream solid – wet
7.15 g – air dry → (4.47 dry)

17.5 free OH xtal

9.07 pre KR

0.4 mm

flip into CH_2Cl_2, dilute base – slow solution between acetone 17.5 g ~~[struck out]~~ CH_2Cl_2 & aq. base. finally two phases – separate
↳ CH_2Cl_2 phase (~300 ml) – strip (9.07 g) – into 100 ml KR
distill 0.4 mm.
80°, 105° no cloudy 140° yes → 170°. ~~[struck out]~~ some pot residue? T to up to 90/140 volts.

80° no
105° cloudy.
130°
140° start.
150° heavy
170° done?

4.47 g dry solids

xtal c̄ 100 ml H_2O | xtal c̄ 150 ml H_2O → combine
→ xtal c̄ 2×50 ml CH_2Cl_2 → nothing ←
let evaporate outside
(let evap.)

residues
↓ filter.
↓ wash c̄ H_2O
↓
much xtal (lots) → dry wet =
↘ small amt c̄ acetone evap
↓
xtals
4.42 wet (to 69)

4.34 g cream oil.
MT.
xtallizing.

4.34 g distilled oil, to xtals

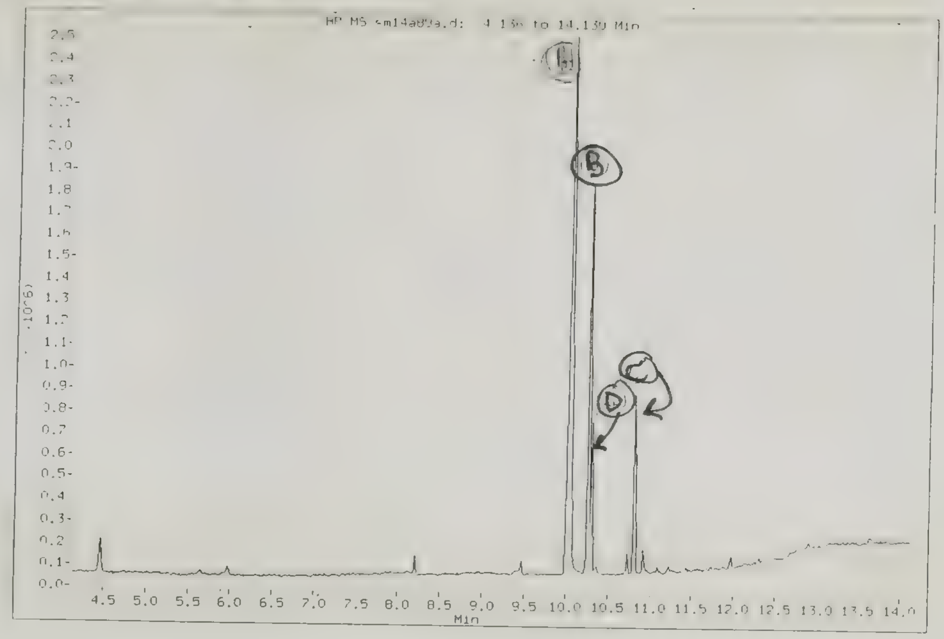
~50 mg under hexane
↳ hexane (66A)

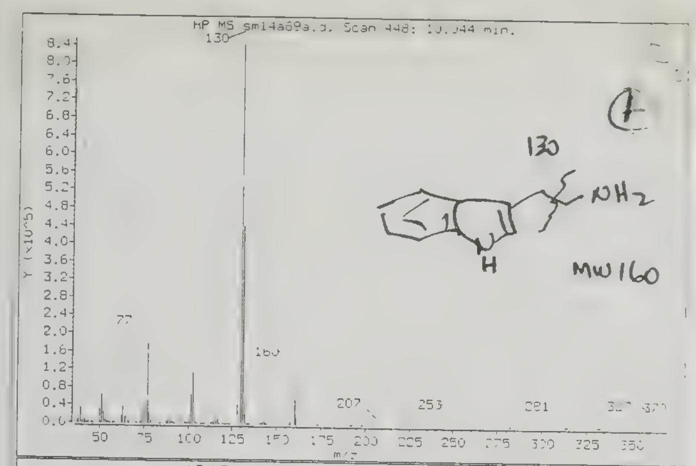
hot dry ethyl acetate → white xtal

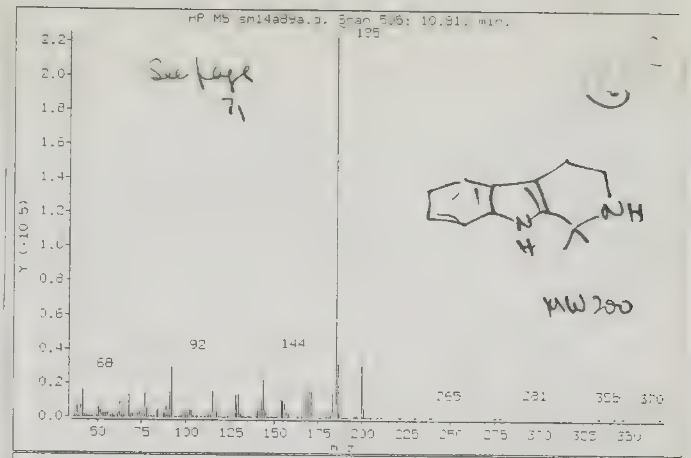
Under went ↳ sol. out. (66B)

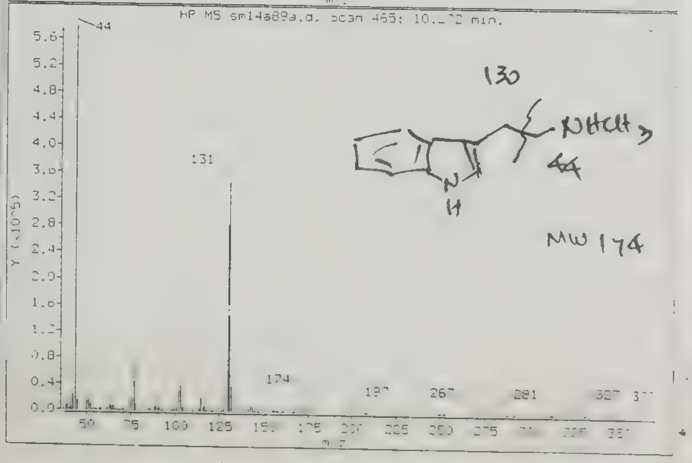
see 107

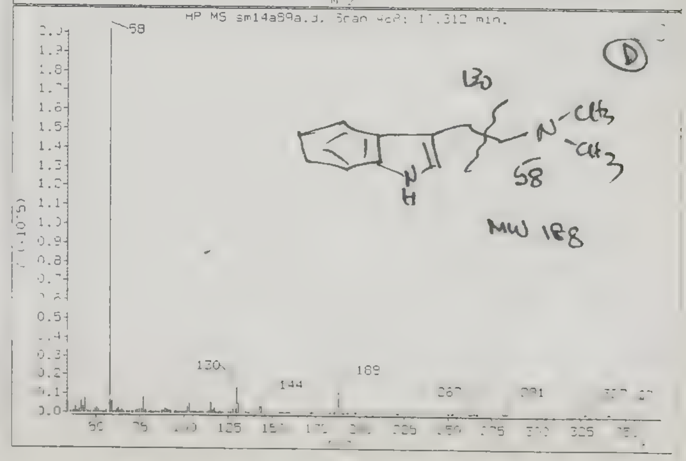
Data File: /hem msd1.1/sm14.b/sm14a89a.d
Injection Date: 12-FEB-96 16:09

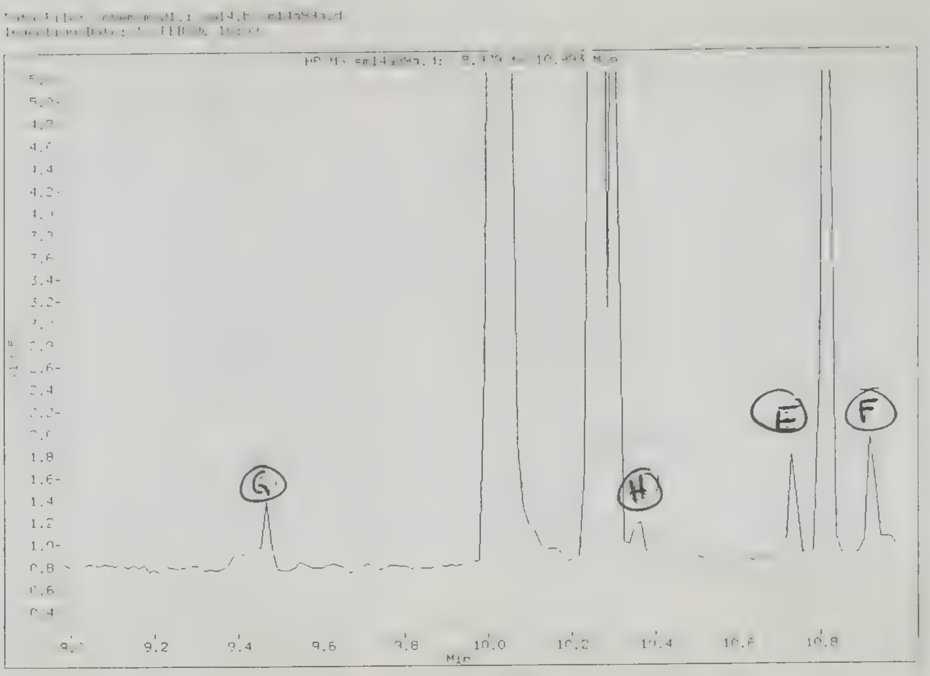


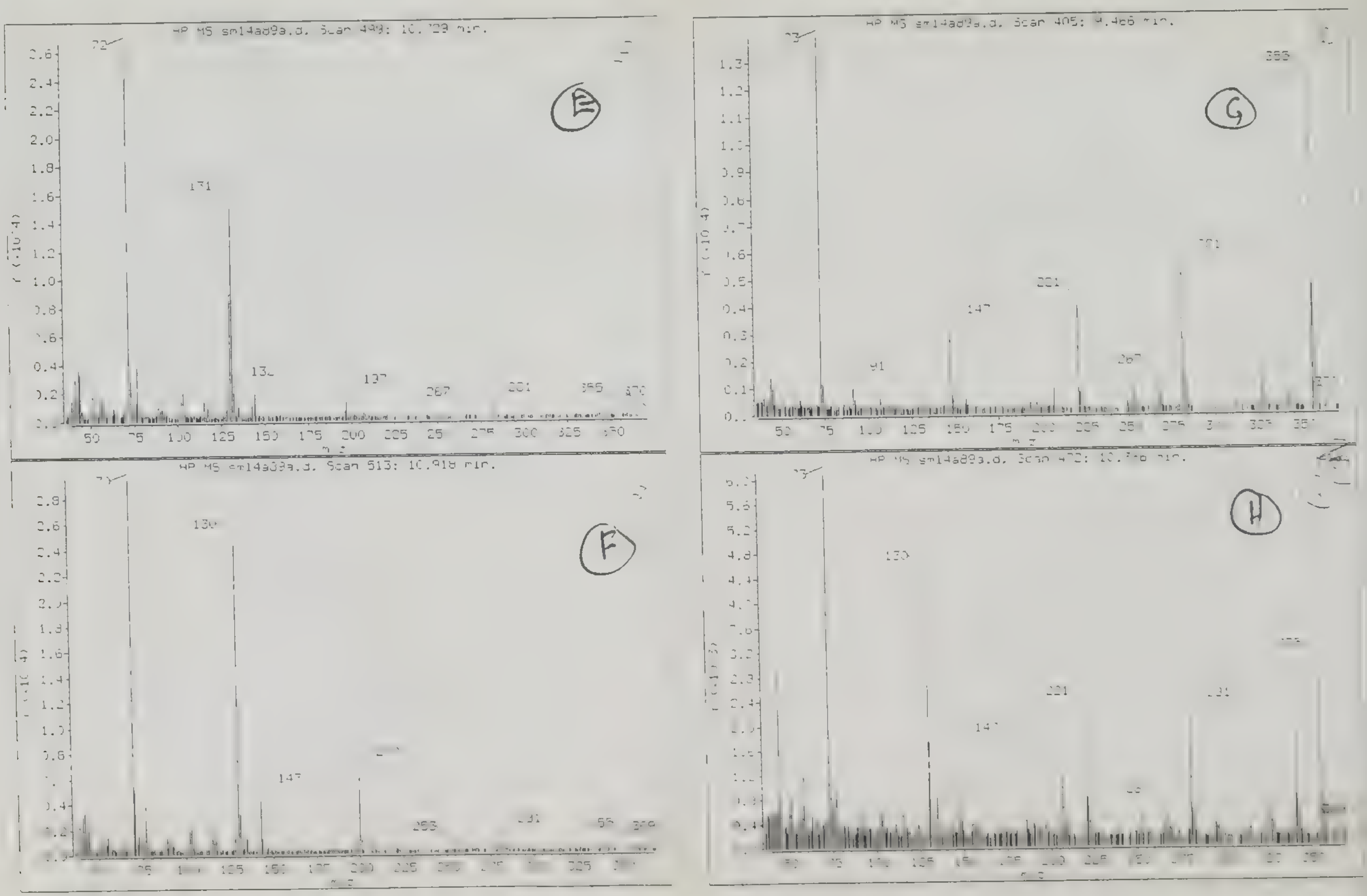


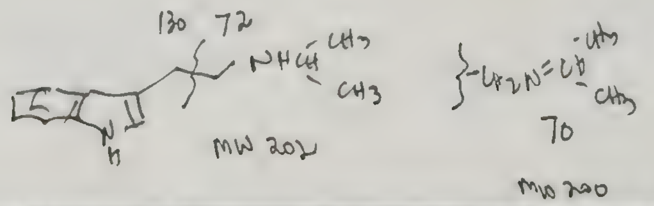







G
H
E
F
Min


E
G
F
H


130
72
MW 202
70
MW 200

Solids from tryptamine + MeI

4.42 g wet. this has been twice extracted c̄ H_2O.
water insoluble

into 2 × 20 ml boiling IPA – separate

Soluble

0.26 g grey solid.
when dry
0.24 g. grey solids.

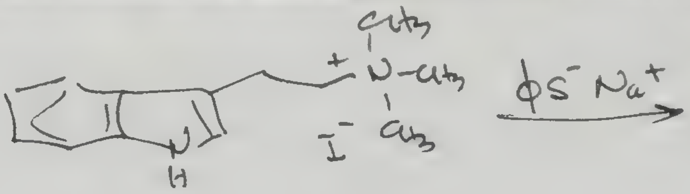
insoluble.
filter – suck –
3.55 g insol.
when dry
2.40 g white solids.

⟷ IR spectra identical

NH 3400 cm^{-1} sharp.

fingerprint { 767 large; 919, 953, 978 } medium — in file

Small amount of each – fused c̄ torch → black tar c̄ tryptamine smell. ~~?~~ – Combine – try $\phi S^- Na^+$



2.64 g quat I^-, suspend in 40 ml MEK. add

{ 1.0 g ϕSH (~10% xs)
{ 1.0 g NaOH (~20% xs) } rinse in c̄ 10 ml MEK.

stir – to reflux at 4^{15} PM.

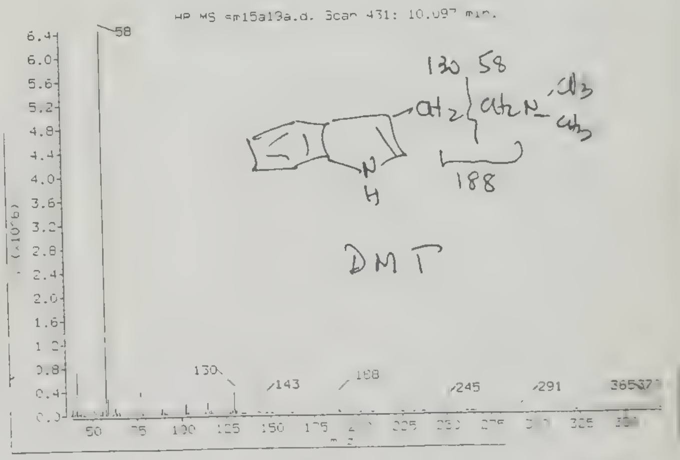
here is my memory ⟷ here is text from recovered notes.

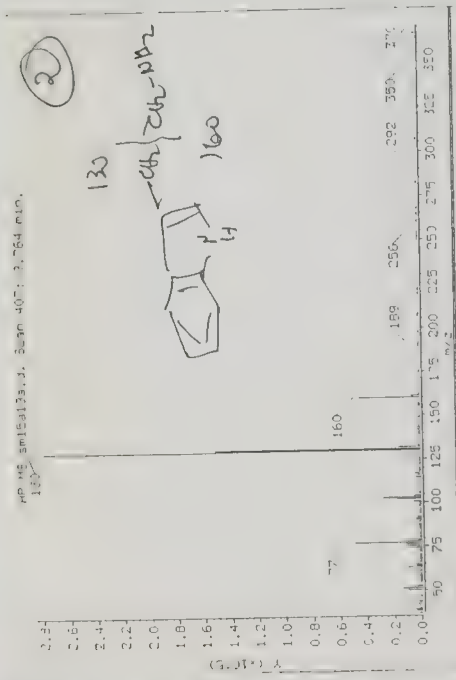
reflux a while (3 hrs? ON?)
strip → residues – into H_2O, basic c̄ strong NaOH – xtrct CH_2Cl_2 – strip → residues –

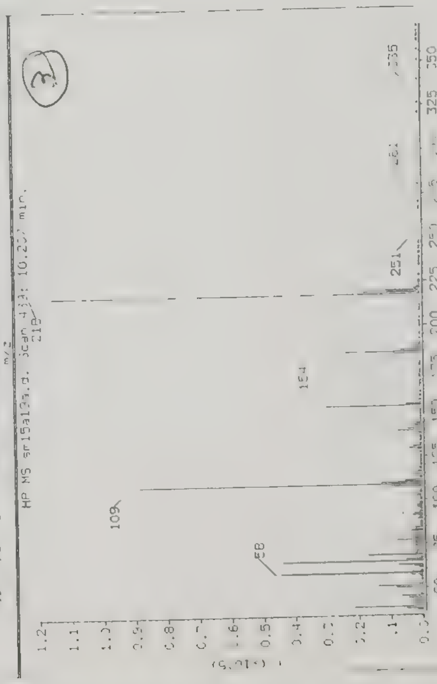
KR – → reasonably high boiling fraction – white oil – weight ~ 0.16 g. slow, but focal xtals. Try IR – still oil & no spectrum.

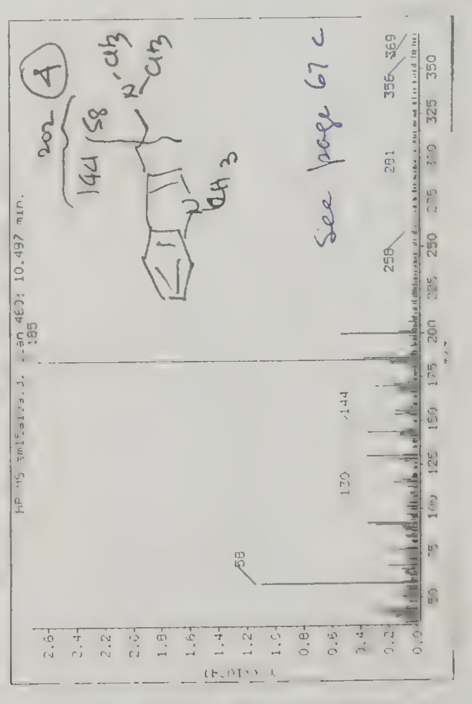
Terrible yield.

70 polym

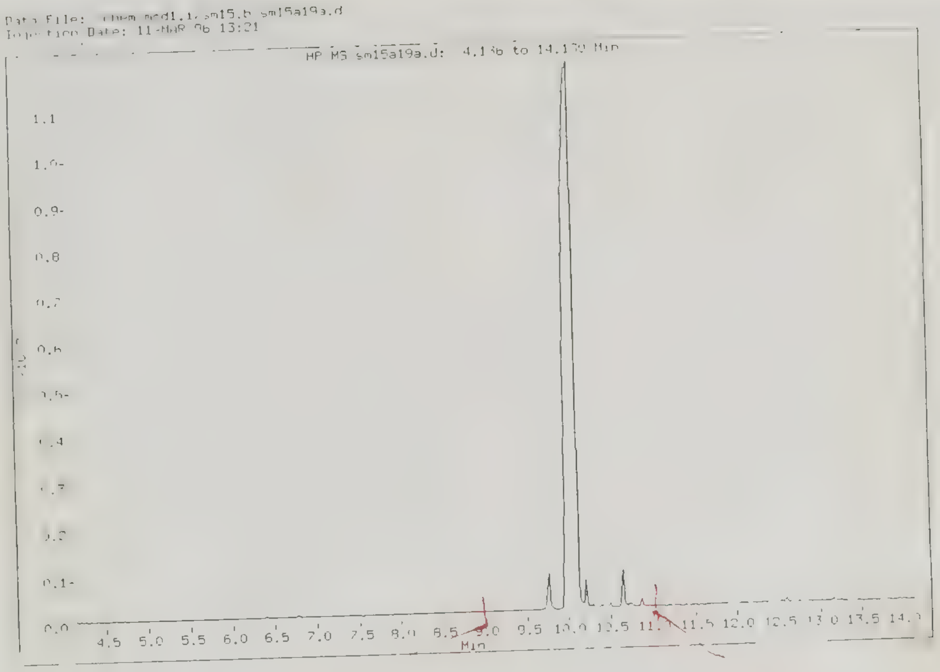








See page 67 c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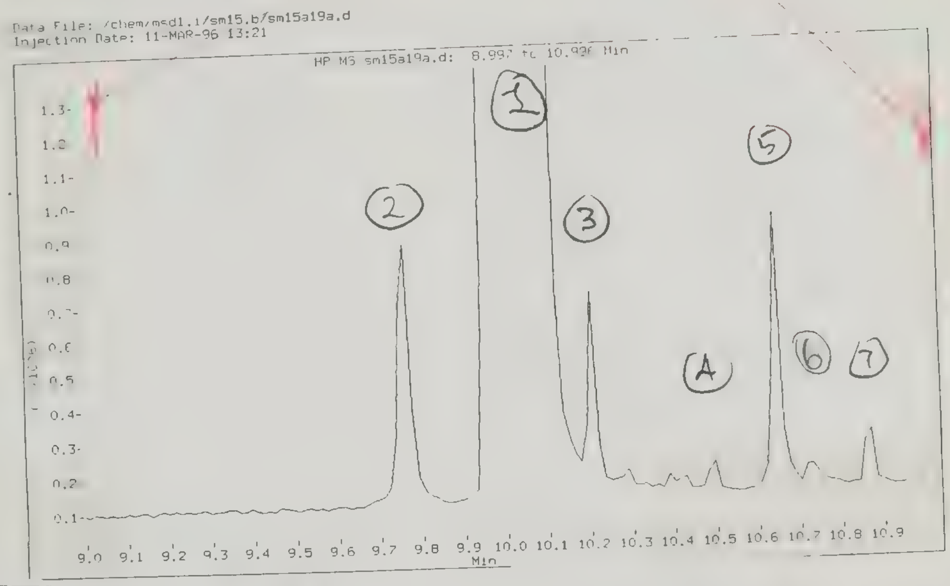
HP MS sm15a19a.d: 4.196 to 14.192 Min
Min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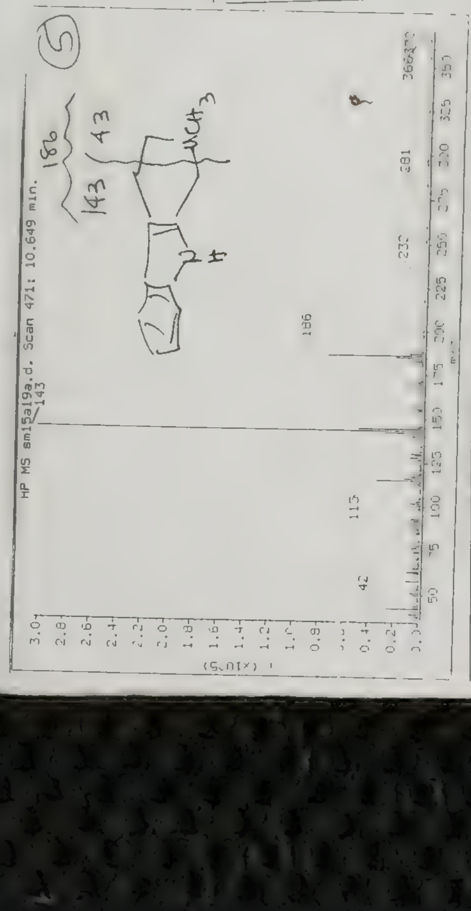
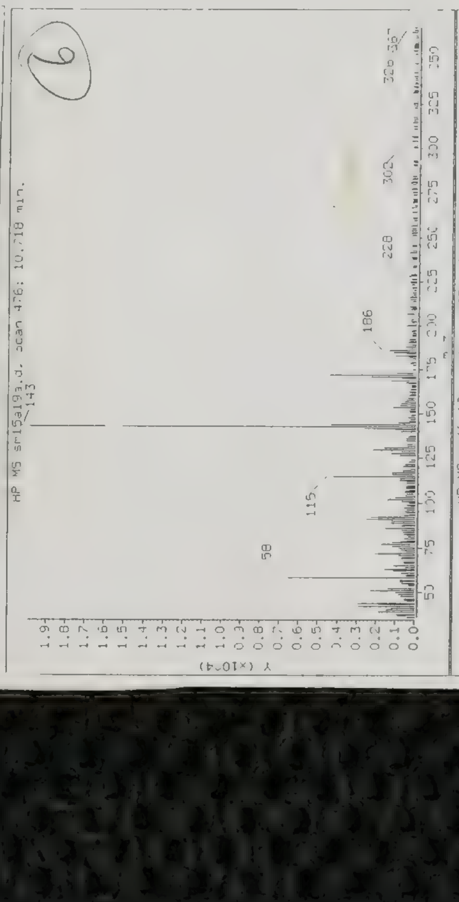
HP MS sm15a19a.d: 8.997 to 10.926 Min
1
2
3
5
A
6
7
Min


5
HP MS sm15a19a.d. Scan 471: 10.649 min.
186
143
43
143
186
113
42
232
281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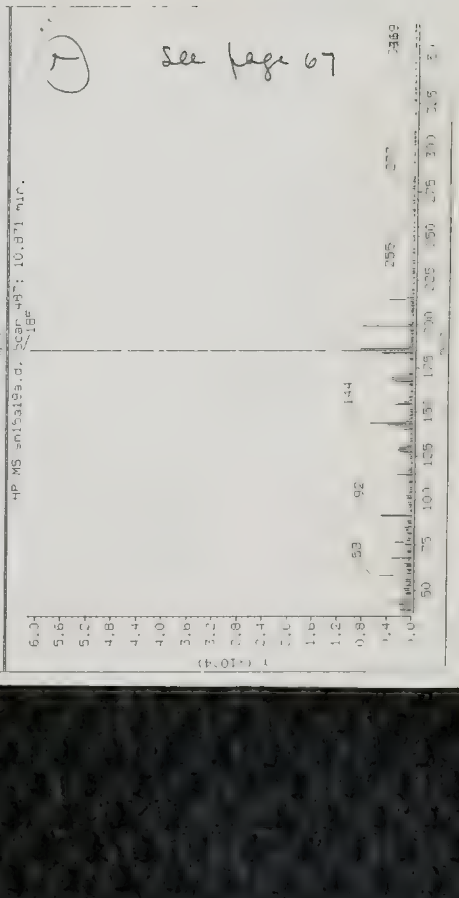
HP MS sm15a19a.d. Scan 476: 10.718 min.
143
186
115
58
228
302


7
See page 67
HP MS sm15a19a.d. Scan 487: 10.871 min.
186
144
92
58
255

~~Trichocereus~~
Pachycereus pringlei

Data File: /chem/msd1.1/T3522/T3522/sm15a19a.d
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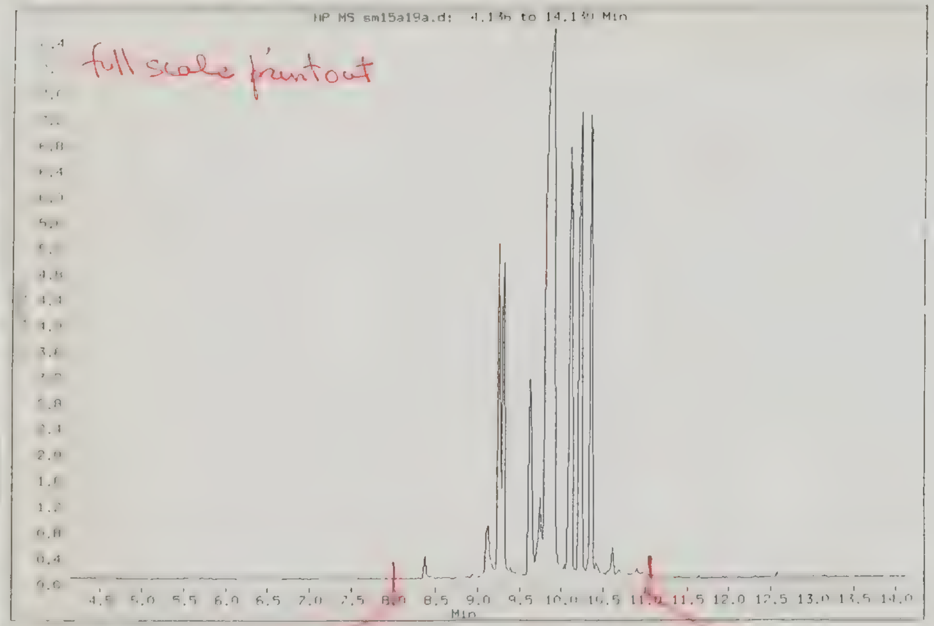
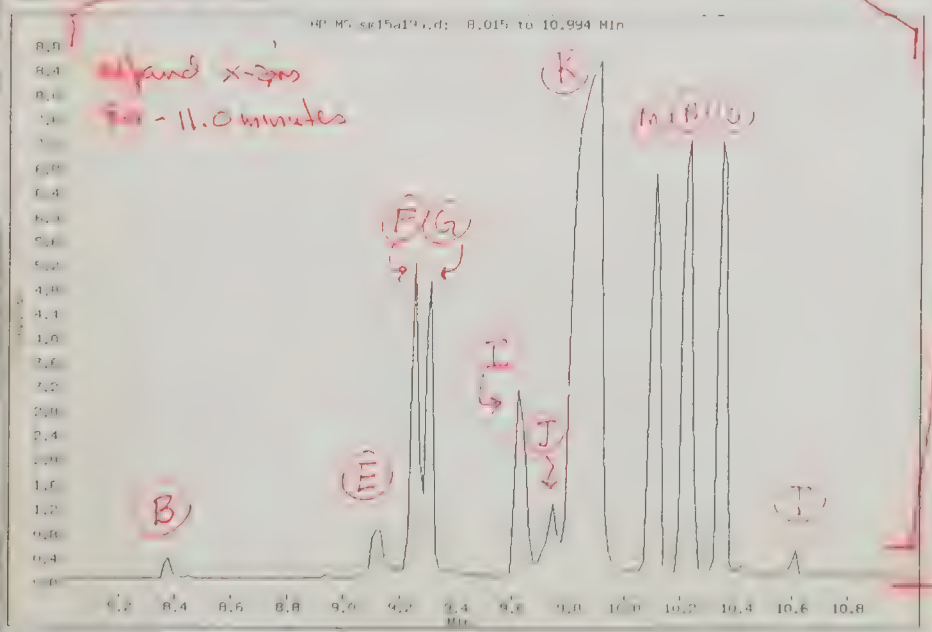


Total extract 1 part P.p. aqueous
1 part 6 N NaOH
1 part

Data File: /chem/msd1.1/T3522/T3522/sm15a19a.d
Injection Date: 11-MAR-96 14:55



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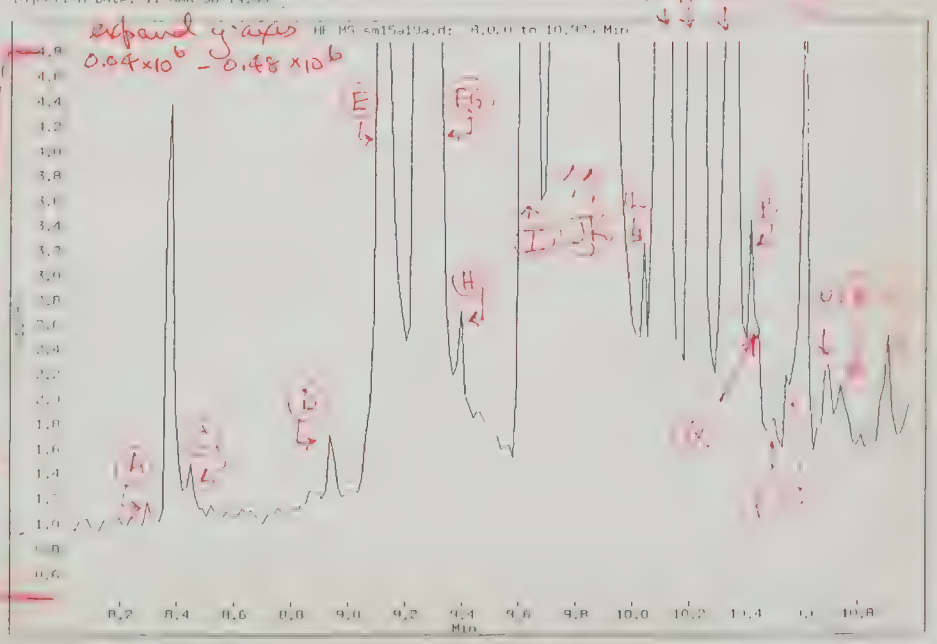
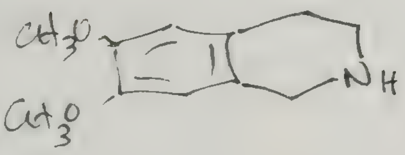
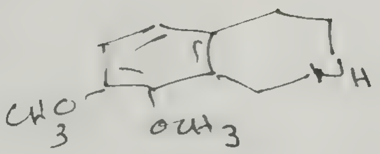


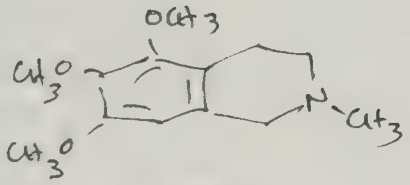
Compounds reported in P. p.



MW 193 Heliamine

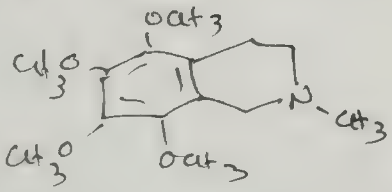


MW 193 Lemaireocerine



MW 237 Tehaunine

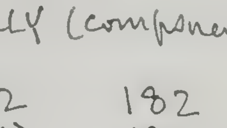
PMCM reports N-oxide MW 253



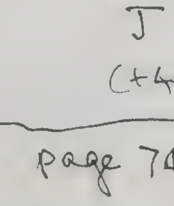
MW 267 Weberine

all by Meta, R. & McLaughlin, J.L. Planta Medica (1980) 38 180-182

note - from M-8501



44 m/z Big
base peak = parent



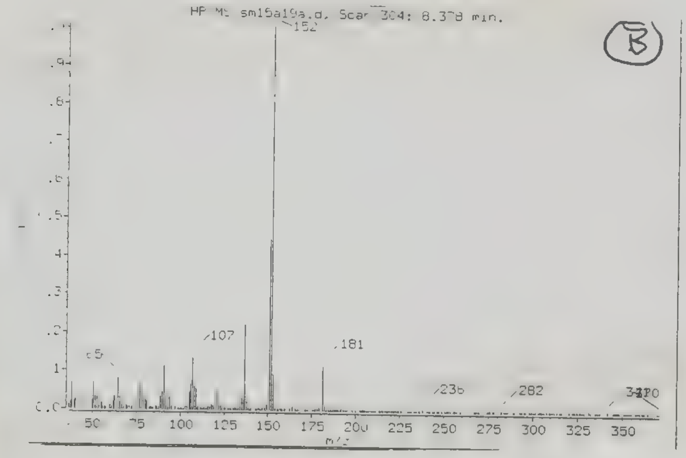
44 m/z Small
weak 30

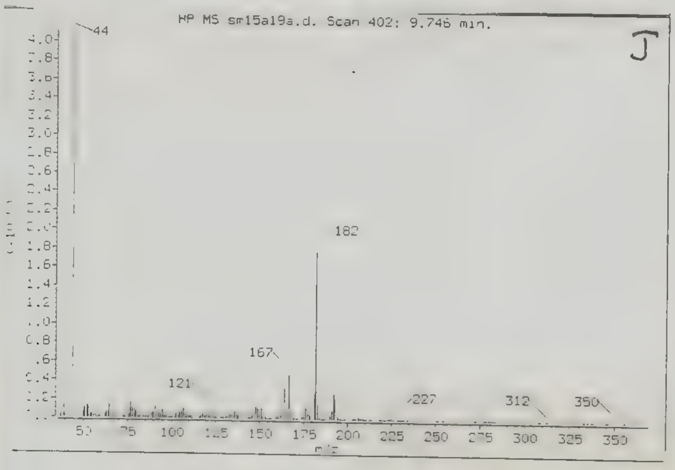
MW TALLY (components)

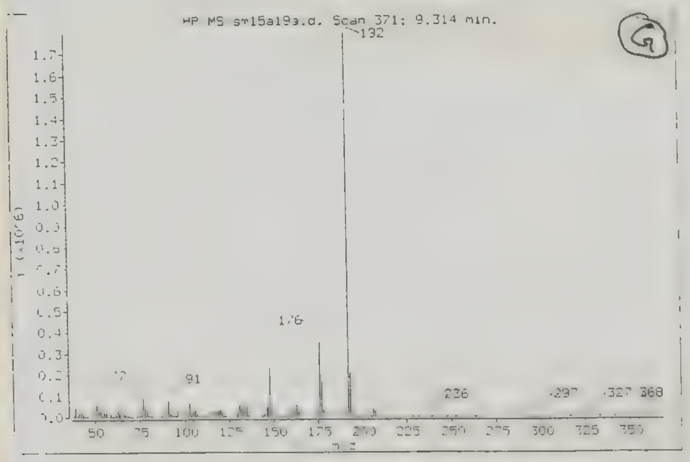
152 (181)	182 192-3	192	206-7	(267)? 219 (236)	236	266
B	J (+44)	G	EFI (K)	T	MN	O
page 74	page 74	page 74	page 75	page 77	page 76	page 77

74

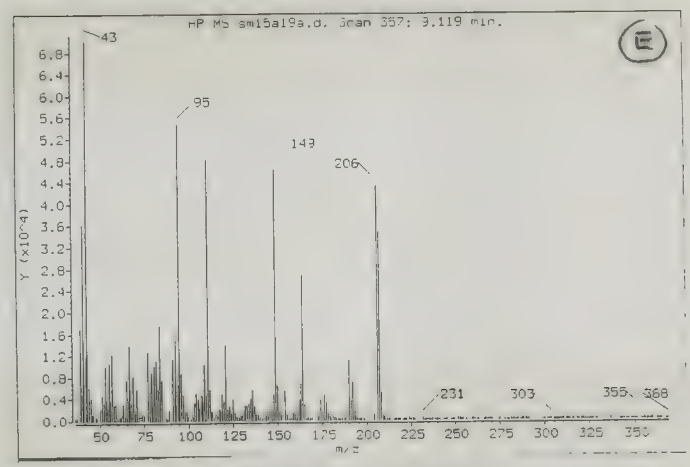
lower MW components

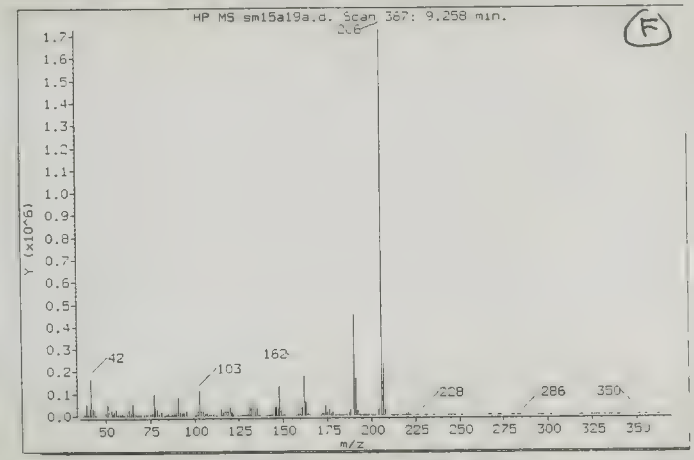


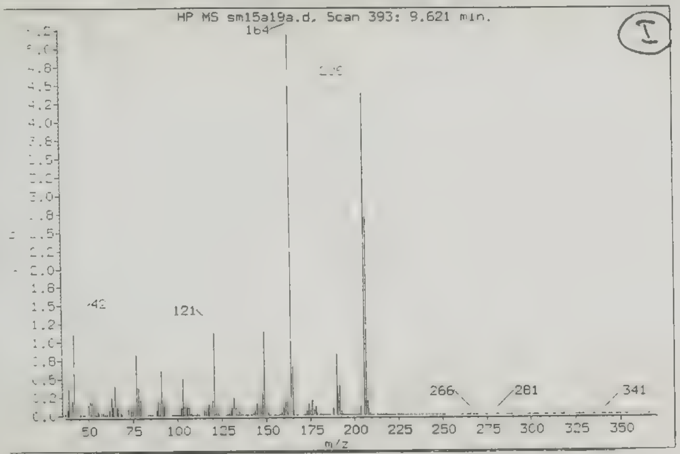


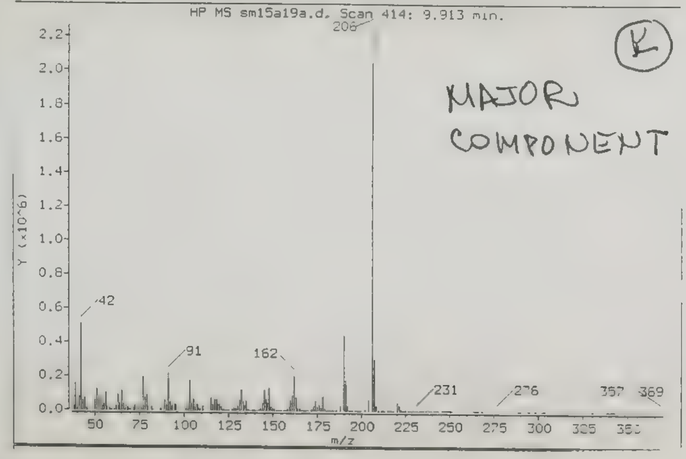


206-7 MW components



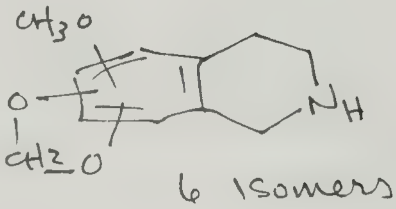




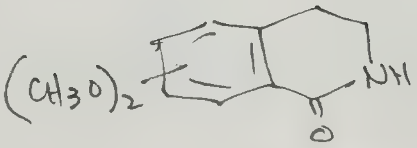


possibilities

12 isomers



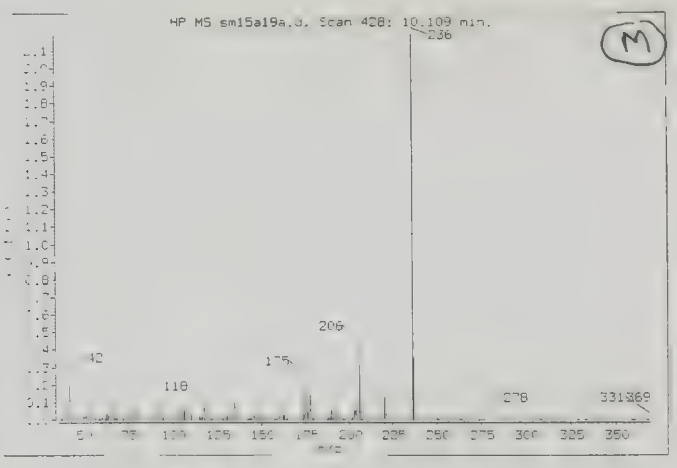
6 isomers

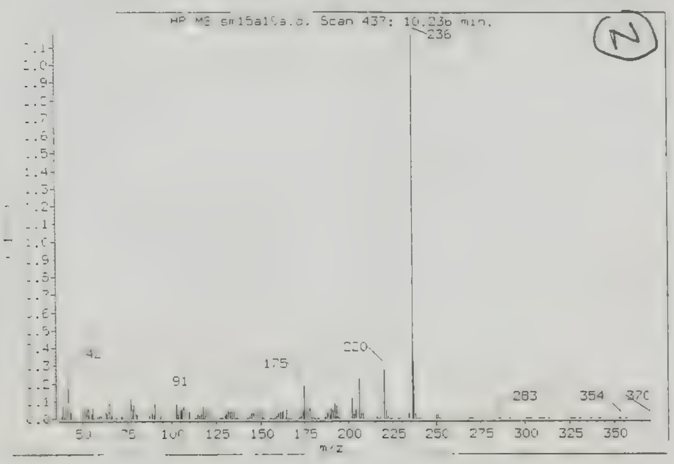


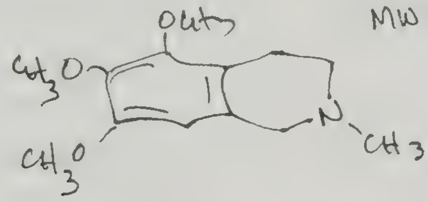
6 isomers

none of these have been reported in P. p.

(76)

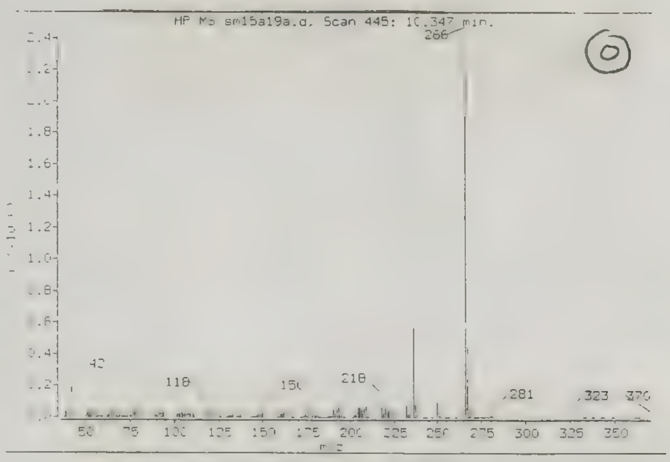




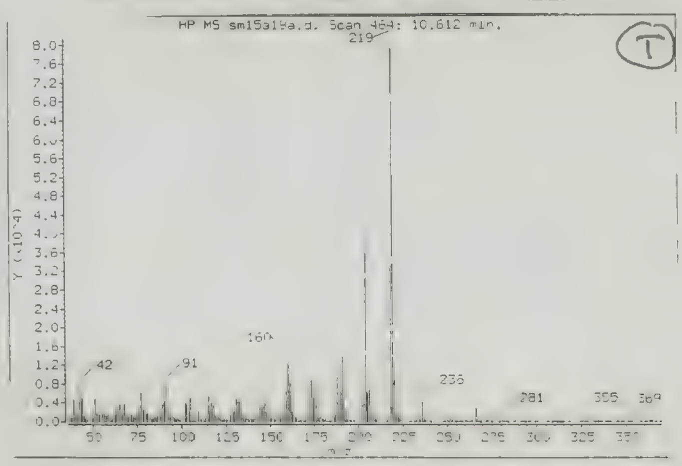


MW 237

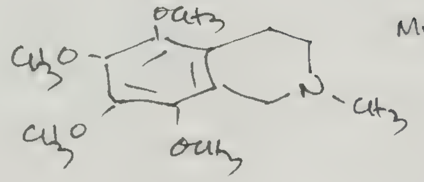
Tehuanine is a reported component of P. p.



MW 266

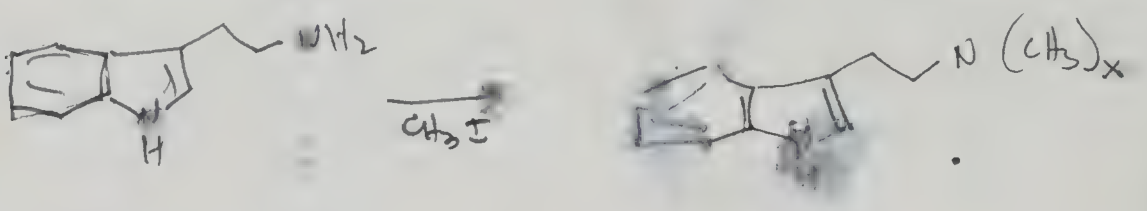


MW 219
236
266?



MW 267

Weberine is a
reported constituent
of P.p.



10 g Tryptamine – into
200 ml CH_2Cl_2 – stir a long while → 1.4 g insoluble
save as recovered T.

8.6 g T. acid.
11.0 g CH_3I – stir 3 days → gummy solid
decant CH_2Cl_2

scrape out goop. 15.84 g.
xtal c̄ IPA – filter –
wash c̄ IPA

CH_2Cl_2
~ <1 g oily stuff – out

→ evap. R.T.
black oil + big xtals
wash c̄ 10 ml heptane – no action
wash c̄ 3 × 10 ml CH_2Cl_2 – color, yes

visual

white solids
wash c̄ IPA
↓
white solids 3.40 g

heptane
CH_2Cl_2
orange organic.
flash → 2.63 g clear liquid.
↑ just heptane – nothing here

black goop
let dry.
6.4 g sticky tar.
grind under 2×5 ml CH_2Cl_2

tar goop
Goop

evap

white solids quat HI = 330 mw.
when dry 3.05 g
dissolve in 35 ml hot water
cool → xtals
filter, wash a bit c̄ H_2O
suck air – dry = 3.07 g

0.3 g – 2 ml acetone
very little. Best

2.77 g

$-CH_2OH$.

⟶

2.50 g quat - dry - into 25 ml MeOH - Δ SB → clear solutin
∇ to RT - gorgeous white xtallization (save a bit on plate)

Δ again - soln. add

1.0 g Ag_2O (10% xs) - looks like white solids (quat, wet AgI)
Δ again on SB ~ 10 min.
Filter - wash c̄ boiling MeOH (another 20 ml). to
slightly opalescent yellow brown solution, add

1.0 g ϕSH. opalescence dissolves. strip on RE. → 2.12 g
viscous oil. Δ c̄ flame - mild reflux (ϕSH?)
but a lot of bubbling. 5 min. ∇ - fine color.
wash c̄ CH_2Cl_2 into beaker - + 50 ml CH_2Cl_2 - xtract
2 × 25 ml dil HCl → aq. c̄ nice yellow color - add
5% NaOH to pH blue - cloudy!! - xtract c̄ 3 × 20 ml
CH_2Cl_2 pool - flash → amber oil 1.04 g.
Slight ϕSH smell. to KR.

1.04 g
115°
2 mm
no
145°
1.5 mm
over
170°

Over at 145° (ufp) 1.5 mm Hg - first colored,
then white! Something funny c̄ vacuum.

5g tryptamine – into 25g MeOH Δ sol ∇ RT

5g 37% CH_2O pH very green.

2.5g $NaCNBH_3$ - stirring – pale green pH → sl. green
quite exothermic; ∇ c̄ running H_2O – add
50/50 conc HCl/MeOH until pH ~ yellow. It does not
AM – still yellow! strip RE → reddish thin
oily sludge

9.6 g tryptamine (60 mM) into 100 ml MeOH add
34 g CH_3I (4 eq.) (used 42 g) - add
40 mL 25% NaOH - - onto SB - reflux → solids, off at 4 hrs; ∇
filter → 52.55 g sloppy wet xtals.
dissolve in 100 mL boiling MeOH, ∇ in ice → pale cream-colored xtals
filter, wash sparingly c̄ cold MeOH - air dry
→ 12.75 g cream xtals

12.75 g into 100 ml MeOH
+ 5.0 g Ag_2O (3.2 I have, 2.0 from) → 3.80 g $AgNO_3$ into 40 ml H_2O + NaOH 2 → 2.4 g Ag_2O
stir - stand a few days - filter - wash c̄ MeOH) → amber fluid.

+ 5 g ΦSH
flash → 8.97 viscous amber oil. In trying to dissolve into CH_2Cl_2 to get into a KR flask, bubbles, exothermic, and eventually 2 phases in CH_2Cl_2! NOT spontaneous ΦSalt ↑ but surely acid & base something!? into small flask. flash on R.E.
Total residue (2 phase, still?) to KR. 0.15 mm - over at 130° → white oil. push to 170° - terrible residue pot → 5.33 g amber glass out
2.18 g watery fluid ΦSH smell

140° over.

(82)

Tryptophan → tryptamine

(See) JCS 3993 (1965) ; Bull. Chem. Soc. Japan 11 121 (1936)

2g dl-tryptophan, into
100 g ϕ_2O - under N_2 - Δ c̄ mantle to boil (250°) signs of decarboxylation earlier - 9:00 PM at reflux - all goes totally clear. Pale yellow solution.
9:00 clock start — Let cool - darkens to amber.

→ here from 83B.

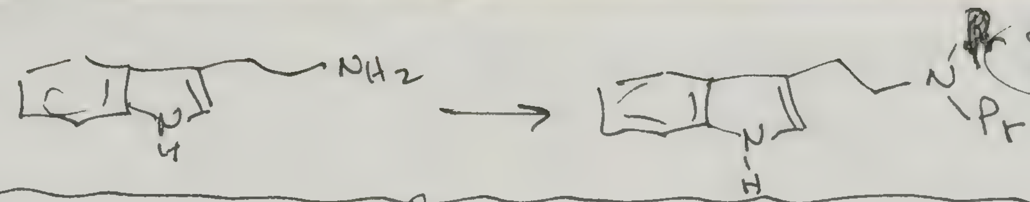
aq. wash 3× CH_2Cl_2

CH_2Cl_2 another → aq. - wash 3×. → aq. combine → again → CH_2Cl_2 - + H_2O + NH₄OH stir, separate flask → viscous brown oil (83B2)

aq. everything thrice washed
+ 25% NaOH → blue, 3 × 40 ml CH_2Cl_2
Strip → .96 g brown oil
KR 145-155°/0.8° → 0.91 g white oil. (83B-3) (bp 146.8° / 155.6°)

to HCl salt (5× IPA, conc HCl, ether) → .88 g salt mp for still → 1.1 g ! mp 174-176 °C.

83



(A) with $NaHCO_3$

1.6 g T (10 mM)
into 20 ml warm IPA Δ, ∇ clear soln
5.1 g n-propyl I (3 fold)
+ 3.4 g $NaHCO_3$ (4 fold

stir RT 36 hrs.
add 100 ml H_2O → pH blue
& black oil
xtrt 3 x 50 ml CH_2Cl_2 - clean
Separation very clean - flash
dichlor → 3.18 g fluid brown
oil - halide smell. (83A 1) (crude tryptamine fraction)
Save a bit for mass spec - TLC
add 5 g Ac_2O. Δ SB 10 min
into 0.5N H_2SO_4. (~150 ml)

aq.
xtrt 3 x 40 ml CH_2Cl_2 → xtrts org.
(some black goobers insol in both)
Keep aq.
+ 150 ml H_2SO_4 sep OUT
aq + ← aq
combine ↑ wash 3 x 40 ml
CH_2Cl_2 OUT — combine flash
+NaOH (6N) to pH blue
xtrt 3 x 25 ml CH_2Cl_2 - flash → 0.41 g

KR, ~ 150-160°/0.5 mm
0.37 white oil (83A - 3)
to HCl salt 5x IPA, HCl, ether
mp 172-174 0.26 g

.8 mm
80°
.5 120°
135° 3 ml
<180° 7 yes
tar
behind

(B) with $(iPr)_2NEt$

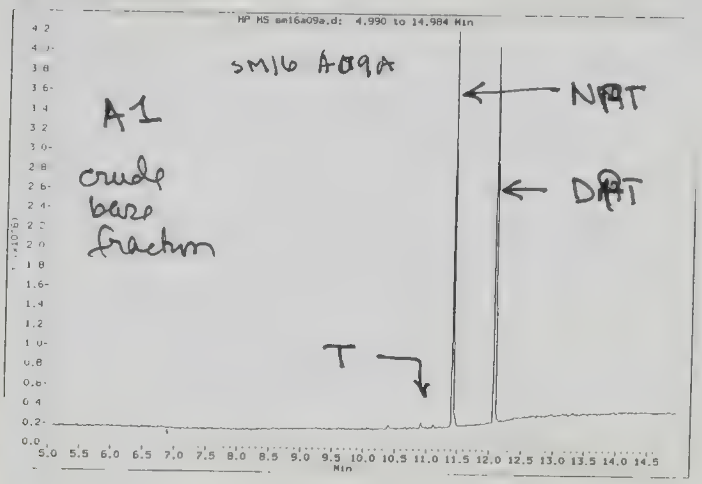
1.6 g T (10 mM)
20 ml IPA ≡
spill 20% (21.6 → 16.7)
+ 4.1 g n-propyl I
+ 4.1 g $(\succ N)_2NEt$ (4 fold)
stir 36 hrs RT
Strip on RE. → 4.51 g
granular black oil
into CH_2Cl_2 + 100 ml H_2O
neutral. OH c̄ 6N NaOH
xtrt → pooled CH_2Cl_2
flash → 2.21 g brown
fluid oil,
(83 B 1)
add 4 g Ac_2O.
Δ SB ~20 min - into CH_2Cl_2
+ 150 ml .5 N H_2SO_4
xtrt aq. 3x CH_2Cl_2 - pool
CH_2Cl_2 c̄ .5N H_2SO_4
wash 2x pool
← O go
- smells of Ac_2O
into CH_2Cl_2 - add
NH_4OH. stir -
Sep. flash again
↳ crude amide fraction (83A 2)

(#84) DPT (bicarbonate)

#83 A

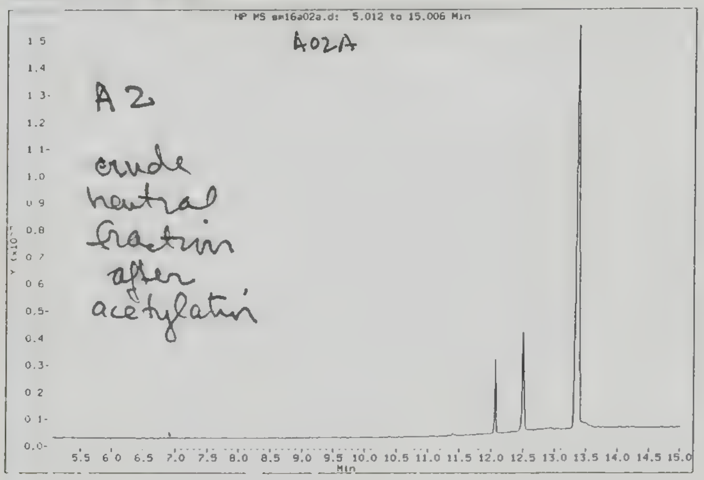
Data File: /chem/msd1.i/sm16.b/sm16a09a.d
Injection Date: 16-SEP-96 20:27

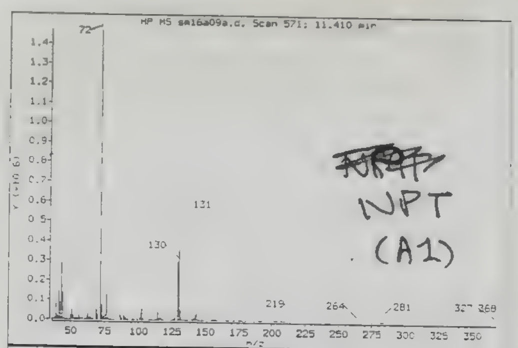
Bicarb

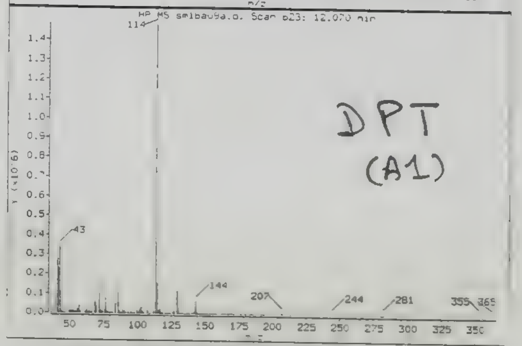


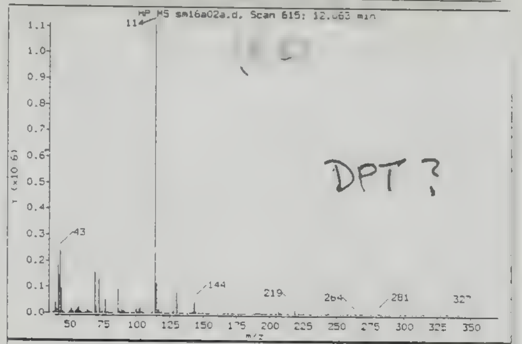
Data File: /chem/msd1.i/sm16.b/sm16a02a.d
Injection Date: 16-SEP-96 17:15

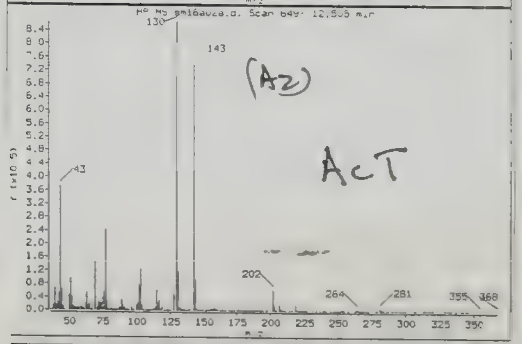
neutral bicarb



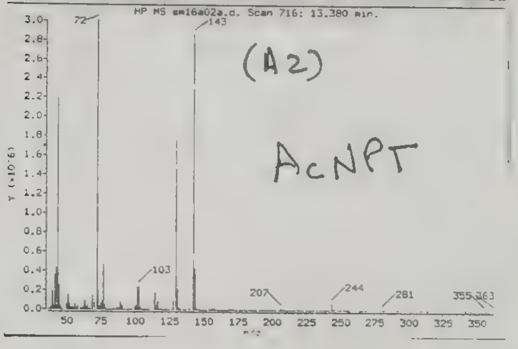








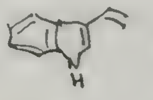
See page 65



$CH_2N(H)CH_2CH_2CH_3$ — $CH_2N(Pr)_2$

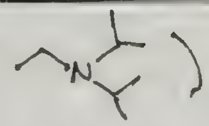
$CH_2N(H)COCH_3$ — $CH_2N(Pr)(Ac)$

72 — 114

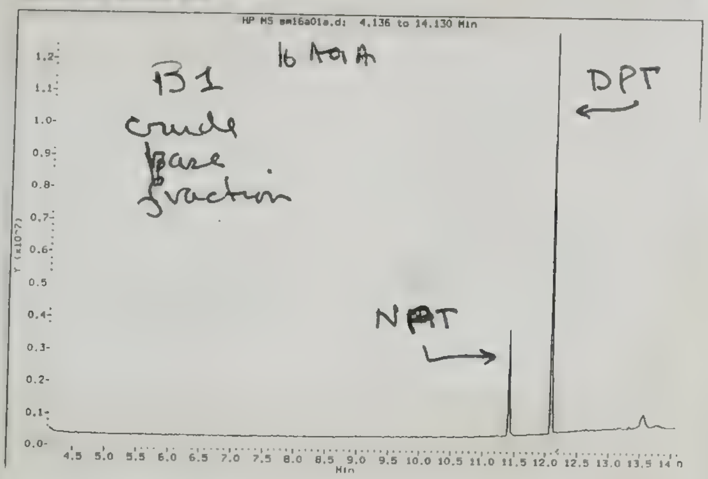


143

parent 244

DPT ()

p 183 B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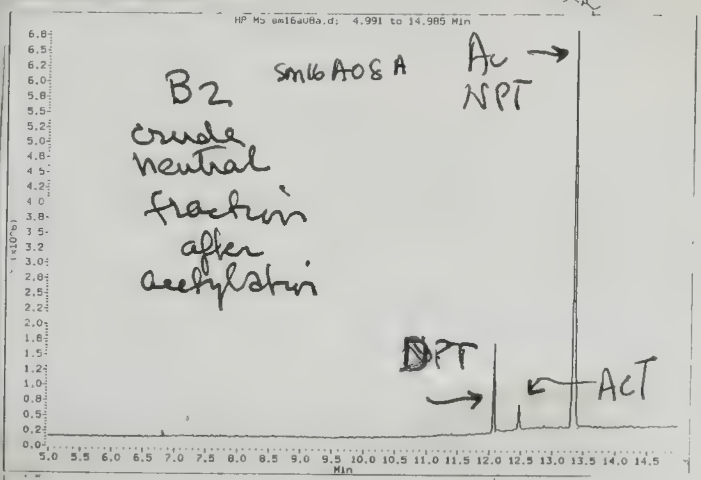
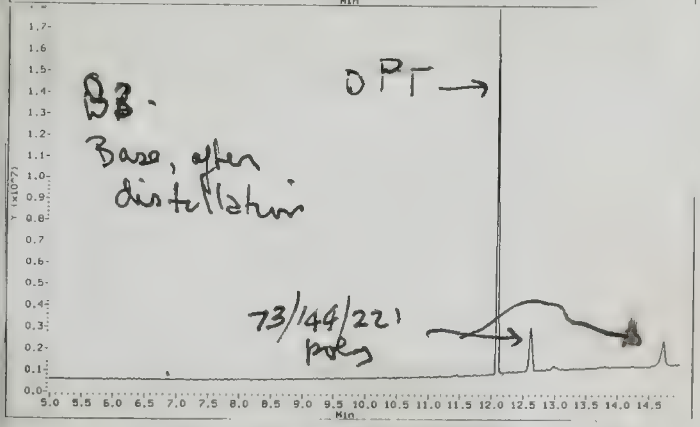
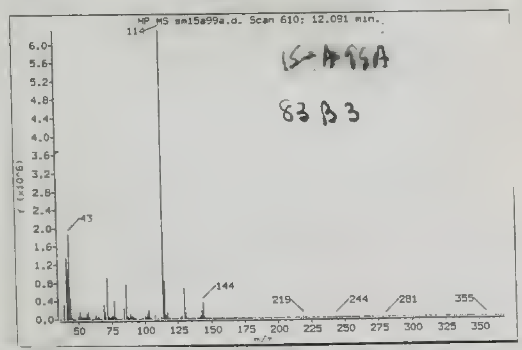
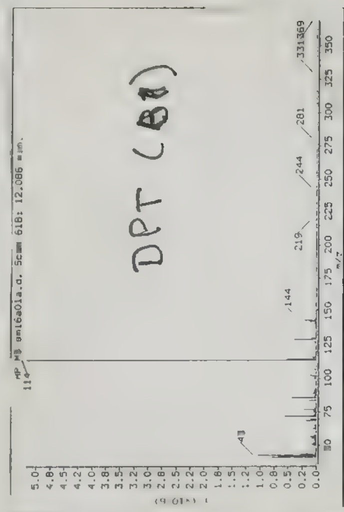
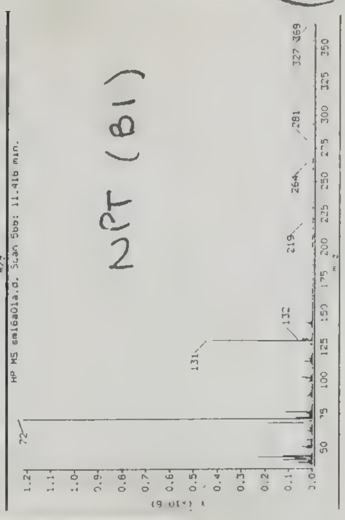
Injection Date: 16-SEP-96 16:46
HP MS sm16a01a.d: 4.136 to 14.130 Min
16 A01A
B1
crude
base
fraction
DPT
NPT

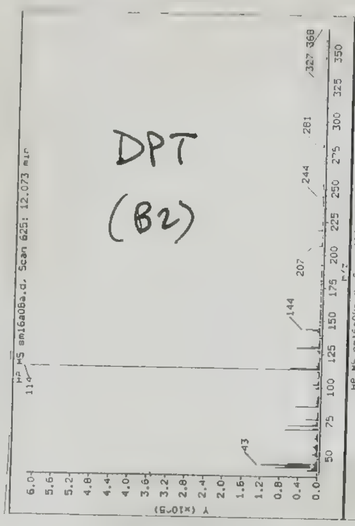

Data File: /chem/msd1.i/sm16.b/sm16a08a.d
Injection Date: 16-SEP-96 20:05
HP MS sm16a08a.d: 4.991 to 14.985 Min
sm16A08A
B2
crude
neutral
fraction
after
acetylation
Ac
NPT
DPT
AcT

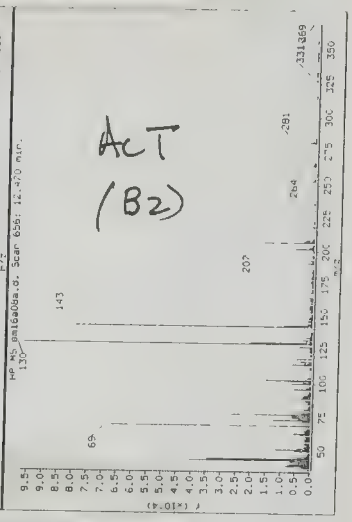

B3.
Base, after
distillation
DPT
73/144/221
poly

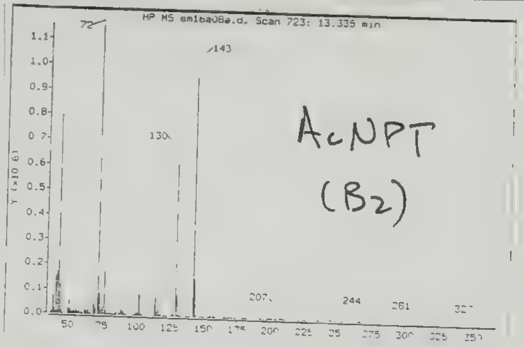

HP MS sm15a99a.d. Scan 610: 12.091 min.
15A99A
83 B3

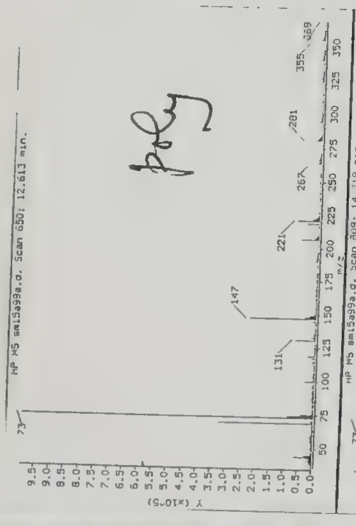

HP MS sm16a01a.d. Scan 618: 12.086 min.
DPT (B1)

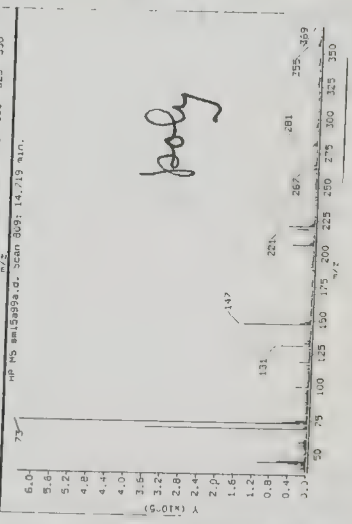

HP MS sm16a01a.d. Scan 566: 11.416 min.
NPT (B1)


HP MS sm16a08a.d. Scan 625: 12.073 min.
DPT
(B2)


HP MS sm16a08a.d. Scan 656: 12.470 min.
AcT
(B2)


HP MS sm16a08a.d. Scan 723: 13.335 min
AcNPT
(B2)


HP MS sm15a99a.d. Scan 650: 12.613 min.
poly


HP MS sm15a99a.d. Scan 809: 14.719 min.
poly

tryptamine $\xrightarrow{EtBr}$?

1.6g Tryptamine base into 20 hot IPA. ∇ RT, add
5.5 ml diisopropylethylamine, add
2.3 ml EtBr (3.3g = 30mM). Stir RT.
add 1.5 ml more base Friday evening
strip Sunday evening - long aspiration → 5.17g viscous light brown
add 5 ml H_2O 5 min SB → RT — save (86A) smudge
add 3.5 ml conc NH_4OH → hot - let cool a few minutes
xtrct c̄ ~150 ml .5 N H_2SO_4 vs 3×40 ml CH_2Cl_2
pooled CH_2Cl_2, another 150 ml H_2SO_4 vs. 3×40 ml CH_2Cl_2

aqueous ↙ — ↓ CH_2Cl_2 stand

OH^- c̄ 25% NaOH
xtrt 3×40 ml CH_2Cl_2 - flash → 1.49g sharp smell -
KR 175-185°/0.05 mm.
↳ 1.02g white oil → white xtals.

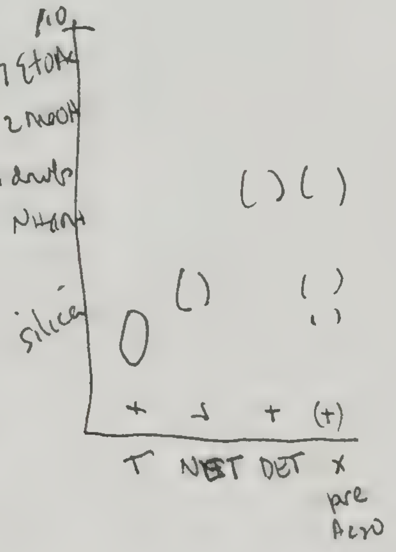
5.49 oil ↓ 5.17 c̄ lots of vac.

2.54 hot hard strip.

1.49 hard strip. Sharp smell

140°/05 no
170° no
175° yes
180° done
185

1.02g, off white in oil



See post distillation - CH_3CN NH_4OH page 94

Mass specs page 96, 97

work-up. scrape out 1.02g white oil
→ 0.92 chunky solid - recrystallize from 20 ml Boiling (almost) hexane
∇ to RT - wait a while → white xtals
filter - wash c̄ RT hexane
↳ 0.72g almost white xtals. mp 84-87°
ML evap

~0.2g into 1 ml IPA - ~ drops conc. HCl. spont. xtals - filter - wash lightly c̄ ether mp 169-171°

tryptamine $\xrightarrow{iPrI}$?

1.6g Tryptamine base, into 20 mL hot IPA - ▽ RT, add
5.5 mL diisopropyl ethyl amine add
3.0 ml (5.1g) iPrI. (30 mm). stir RT.

add 1.5 ml more base Friday evening.
strip on Sunday evening → 3.28 g medium brown oil
add 5 ml Ac_2O. 5 min SB. Δ to RT.
add 3-5 ml conc NH_4OH. → hot - let come to RT.
AM - still acid !!? - add gobs NH_4OH - let stand
next day - partition 0.5 N H_2SO_4 (no, stronger!)
vs. 3x 40 CH_2Cl_2

xtract pooled CH_2Cl_2 c̄ H_2SO_4 vs 3x CH_2Cl_2 40 ml

aq. pool,
base c̄ NaOH 25%

xtract 3 x 40 ml CH_2Cl_2 - flash → 0.20 g ugh.

KR: 170-185°/0.05 → a couple of droplets of white oil SLOW xtals ! OUT

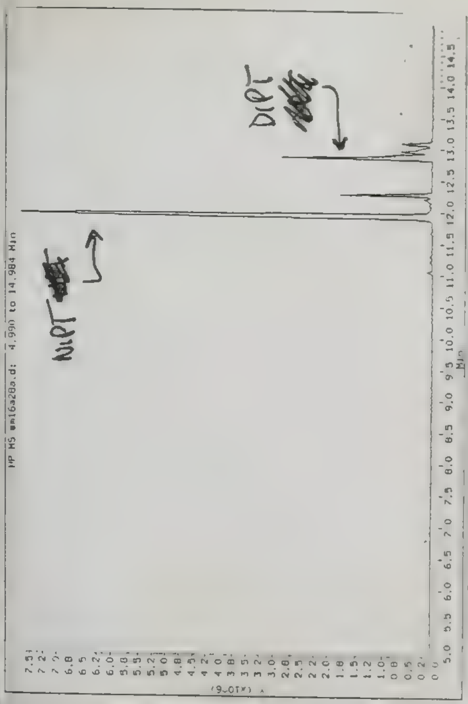
Sol. .742

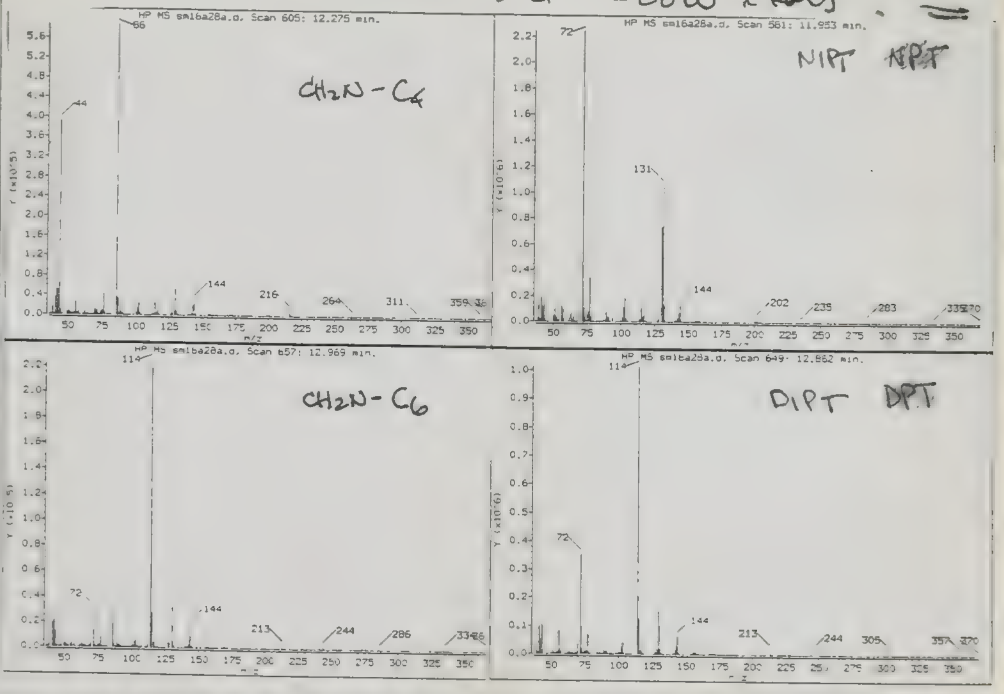
add 3.9 ml

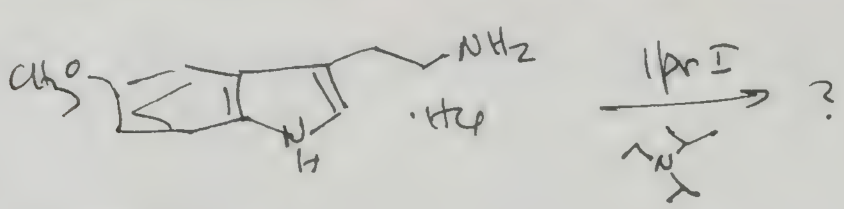
7.0 ml theo x4

pooled CH_2Cl_2 stand

strip 0.20







(1.0 g amine) · HCl MW 226.5 = 4.42 mM
(10 ml IPA)

(4.0 ml amine) MW 129 × 5 = "645" MW
× 4.42 mM = 2.86 g d = .742 = 3.8 ml Δ to almost at RT - add

iprI MW 170 × 3 = "510" MW
(1.33 mL iodide) × 4.42 mM = 2.26 g d = 1.70 = 1.33 ml

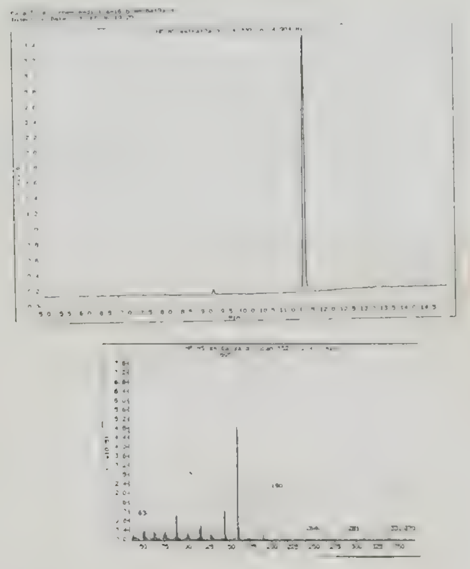
Stir for ~36 hrs RT. - appears to drop out a white ppt - filter solids 0.77 g dry; beautiful · evap ML to residue (smudgy)

Sol
0.77

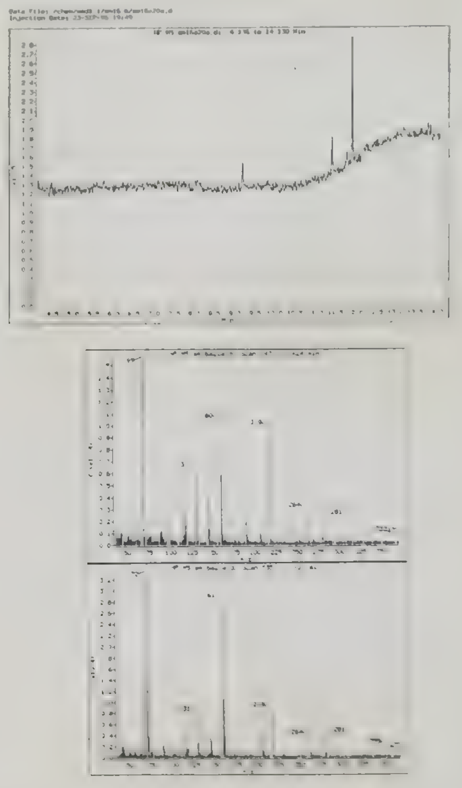
ML
good
Smudge

MW 5-MeoT 160 + 30 = 190
N ip 160 + 72 = 232
N(ip)2 160 + 114 = 274

White solids (160, 190, 1.0)

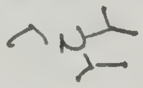


Smudge



Repeat
p87

tryptamine $\xrightarrow{ipI}$?

1.6 g T base into 20 mL IPA on SB. add
7.5 mL  add

3.0 mL IprI on SB 7 PM Tuesday reflux. off noon Friday
strip quite hard → ~ 7.8 g dark mass – I
don't believe the weight Dissolve in ~40 ml
CH_2Cl_2 – wash 2x H_2O, spot a bit of CH_2Cl_2 –
strip. ~~add 200 ml H_2O, more NH_4OH~~ add 5 ml
Ac_2O – Δ 55°/5 min. to RT – Add 5 ml NH_4OH
(not basic after warming at 55° a while –
add gobs more ammonia – basic (*) ~~[illegible]~~)
0.5 N H_2SO_4 to 200 ml, acid.
extract 3 x 40 ml CH_2Cl_2 → CH_2Cl_2 save (89B)
aq. wash 2x40 ml CH_2Cl_2
basic c̄ 6 N NaOH → cloudy.
xtract 3 x 40 ml CH_2Cl_2 – flash – into
50 ml 19/20 c̄ CH_2Cl_2 – flash
↳ 0.96 g brown oil.

~7.8 g

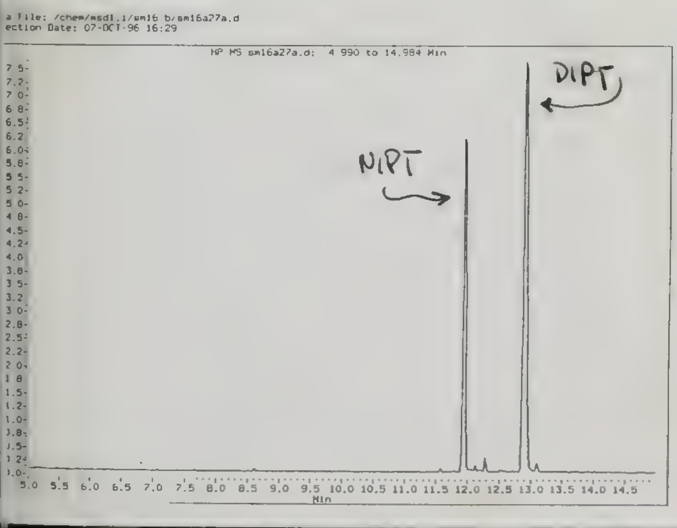
.96 after NH_4^+

~~[illegible]~~ To KR:

0.6 mm 160°-175°

0.85 g off-white oil
pretty much
xtals

0.6 mm
140° no
160° g/s
175° done



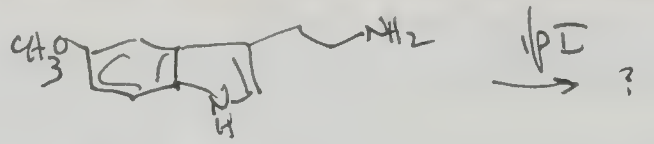
insert (*) add 3x40
CH_2Cl_2 – to extract everything
into CH_2Cl_2 – then xtract c̄
dil H_2SO_4 BUMP – lose 20%

→ dug out = 0.91 g !?
grind up under 10 ml RT hexane
filter

0.31 white xtals (89D) + pale yellow ML let evaporate (89E)

TO PAGE 99

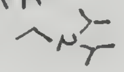
(90) push (88) again



0.77 g white xtals f. p 88 - into H2O (sol) + 6N NaOH → pH > 9
xtrt c̄ 3 × 40 ml CH2Cl2 flash, add all p. 88 scrudge

0.83 g from Rot. Evap. (some xtals forming)

try again, without Cl⁻

10 ml IPA
4 ml 

1.33 ml iPrI use 1.5 ml onto SB 36 hrs

strip to residue (save bit for TLC, MS) (A)

+ 5 ml Ac2O - gets quite hot. did not put on SB. 10 min -
5 ml conc NH4OH. not spontaneous, + lots of water -
more NH4OH - to basic - xtrt 4 × 50 ml CH2Cl2 pool

second smoke. 175-190/.6 .52

xtrt pooled CH2Cl2 xtracts

1 c̄ 200 ml .5N H2SO4 wash c̄ 2 × 40 ml CH2Cl2

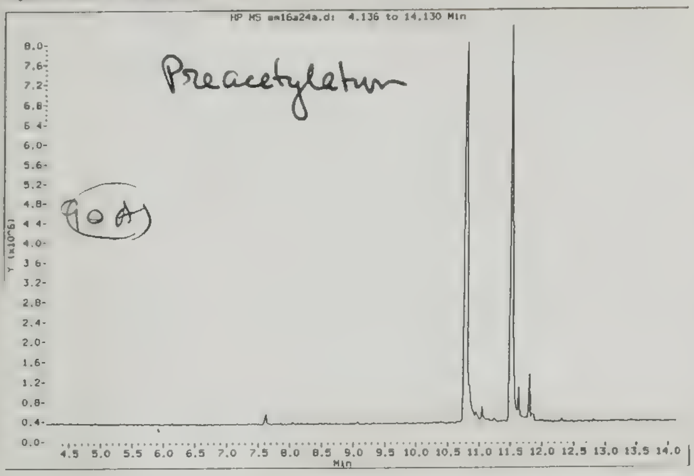
1 again c̄ 200 ml .5N H2SO4 wash c̄ 2 × 40

pool, basic c̄ 6N NaOH (cloudy! nice) xtrt c̄ 3 × 50 ml CH2Cl2

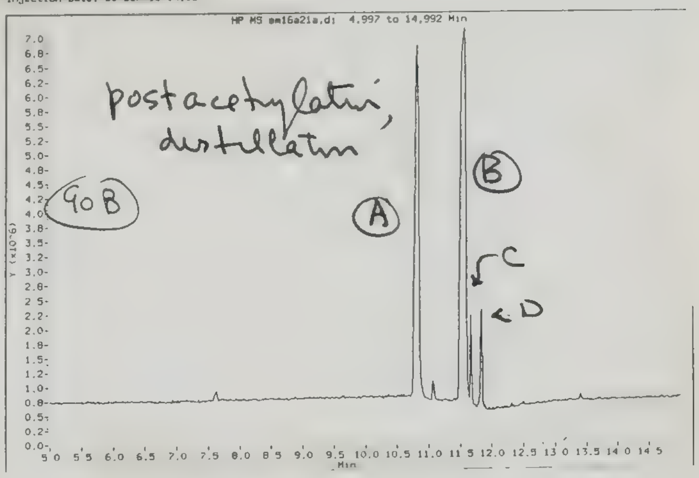
Strip → .86 g crude

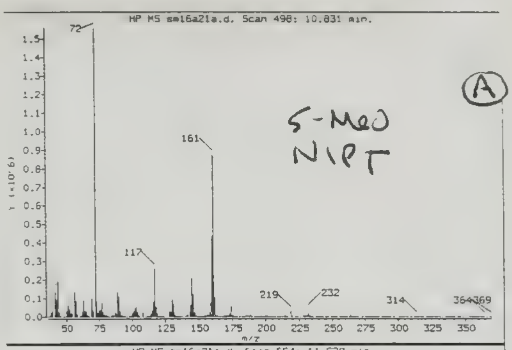
KR 175-190/0.6 mm → 0.52 g off-white oil (B)

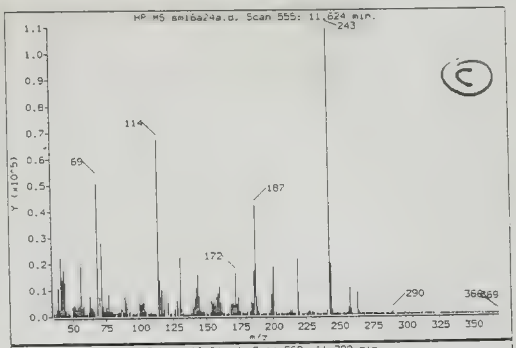
Data File: /chem/med1.i/sm16.b/sm16a24a.d
Injection Date: 30-SEP-96 16:32

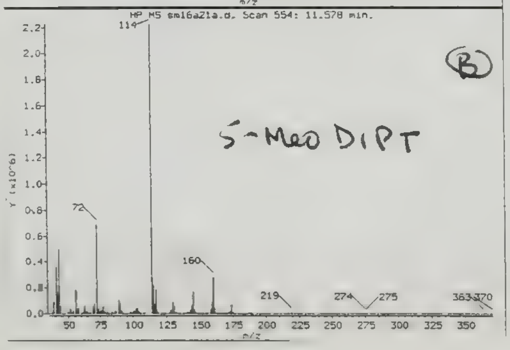


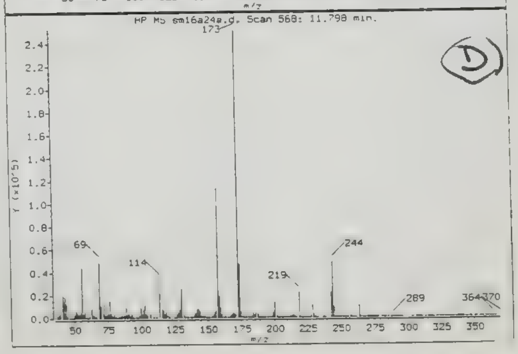
Data File: /chem/med1.i/sm16.b/sm16a21a.d
Injection Date: 30-SEP-96 14:13











(92) push isopropylation harder

all .52 g distilled oil (90B) (small start of xtal - save)
rinse out c̄ 3 g, then 2 g hot sulfolane - not quickly sol
+ .62 g $\sim$ (aimed for .58) (2:1 (as mono))
+ .78 g iPrI (aimed for .75) (2:1 (as mono))
Δ 88 3 hrs → rather dark red-brown.

into 50 ml 0.5 N H_2SO_4
xtrt 4 × 40 ml CH_2Cl_2 → aq

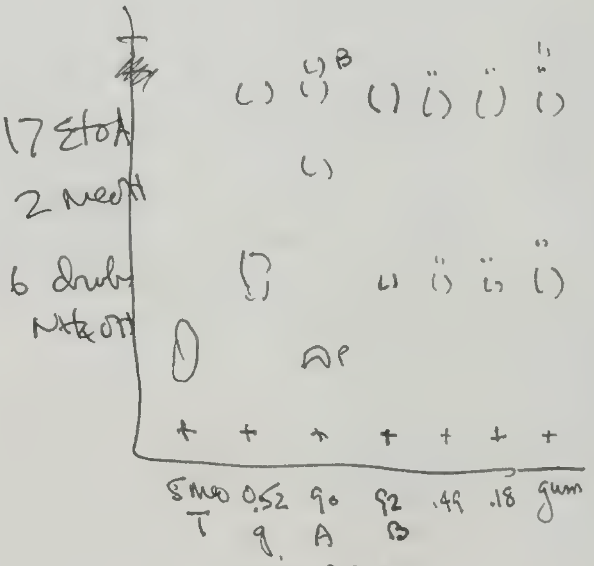
CH_2Cl_2 pool,
xtrt 80 ml H_2SO_4
xtrt 4 × 40 ml CH_2Cl_2 → aq

CH_2Cl_2 pool ←
(92A) ↔ (See page 108)

pool. aq
+ xs 6N NaOH
blue pH,
xtrt 3 × 50 ml CH_2Cl_2

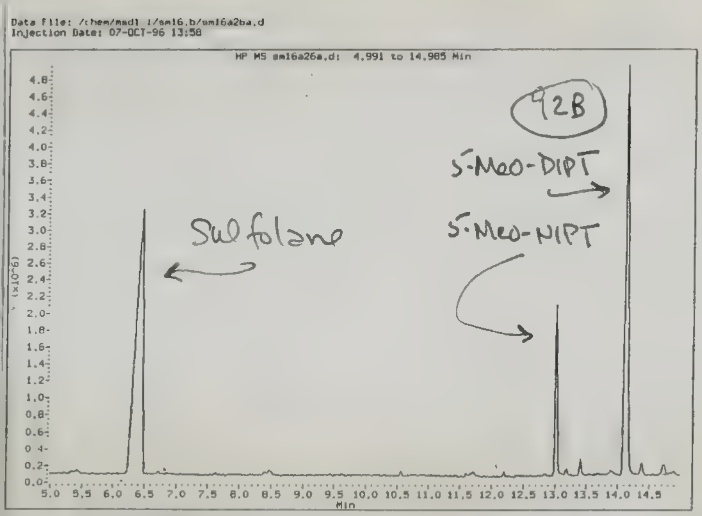
flash → 0.49 g pale amber oil (92B)

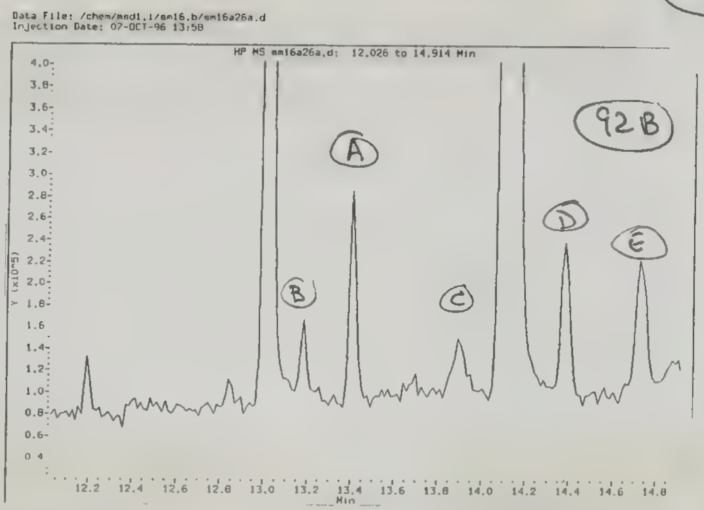
GCMS ~80/20 di iPT + sulfolane
TLC - same - sulfolane invisible
spray c̄ 1% $KMnO_4$ in 0.1 NaOH - invisible
(1 g in 100 ml + 1.5 mL 6N NaOH)

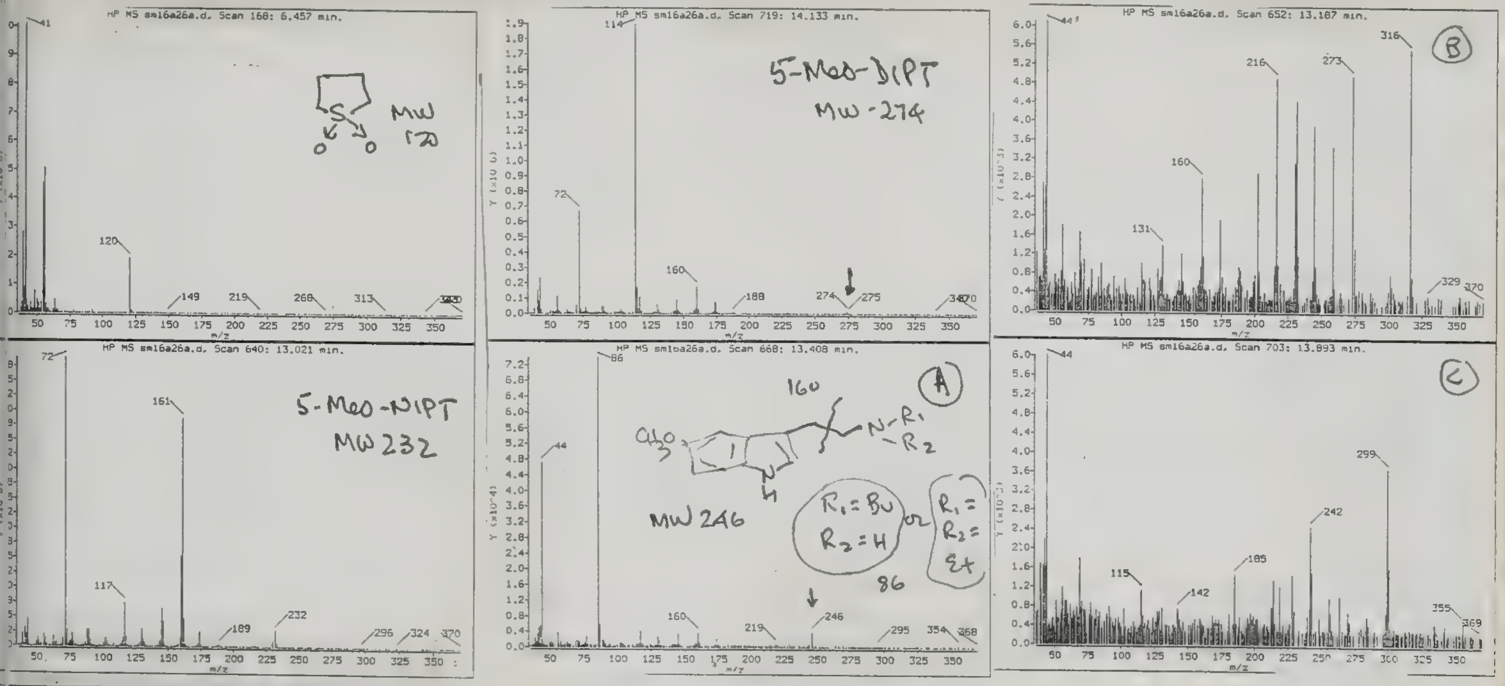


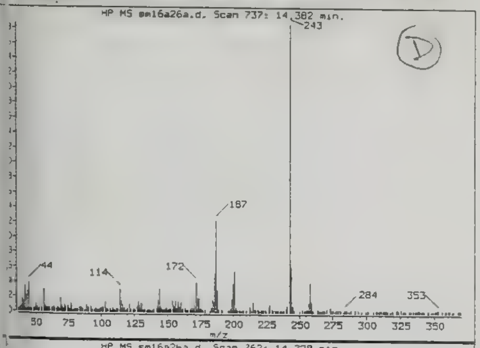
Determine Part. coef. for sulfolane.
1 g sulfolane < 10 ml H_2O / 10 ml CH_2Cl_2
Flash CH_2Cl_2 → .62 g
xtrt 10 ml CH_2Cl_2 → another c.13
∴ partition coef ~ 2 CH_2Cl_2 / H_2O

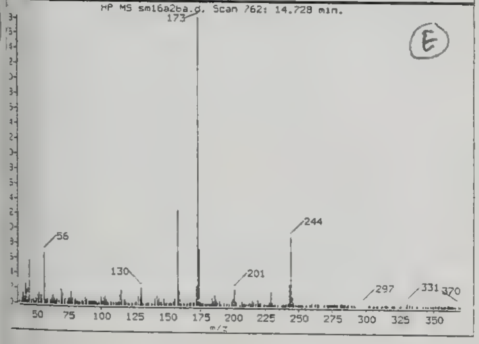
all of 0.49 g 92 B into 30 ml hexane,
30 ml H_2O. - Some few milligrams of (gum)
don't go either way - shake - all color to
hexane. wash hexane c̄ another 30 ml H_2O
flash → colorless oil (0.18 g) ~~.......~~ oil, distilled (92C)
to KR. 150-160° oven.
0.01 mm → 0.18 g white oil
into 0.75 ml IPA + conc. HCl (3 drops not enough, 5 too much)
+ ~1½ ml ether → xtal. filter, ether wash,
air dry. → 0.13 g almost white solid ← Salt, solid (92D)





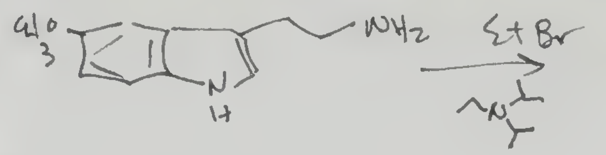






Spectra of 92C
distilled oil
and 92D
Hydrochloride salt
on page ~~93~~ 98

(94) attempt:



(5 mM)
0.95 g 5-MeOT. freebase TCI - beautiful-looking stuff - into 10 ml IPA - Δ on SB to dissolve → RT - add

\+ 2.8 ml [amine] (2.61 ml = 15 mM d. .742 MW 129)

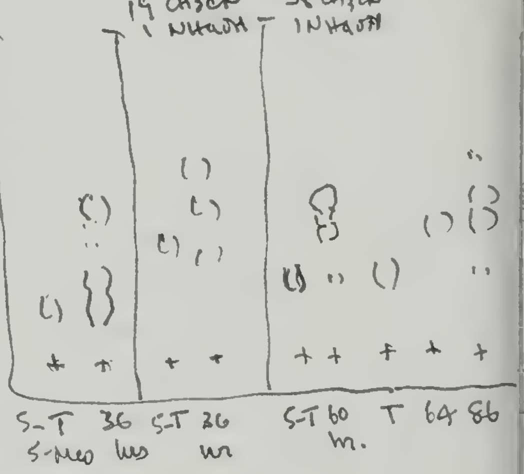
\+ 1.2 ml (used 1.3) EtBr (1.13 = 15 mM d = 1.46 MW 109)

Stir RT 3PM Wed.

36 hrs - all three there still

duplicate + 2.8 ml amine
+ 1.2 ml EtBr

another 24 hrs:
36 hrs.



strip → (94A) 3.49 g save dab. - 2 phases!

add 1.6 g Ac_2O (.51 theo) . onto SB. ~20 min. into beaker - + 3 ml NH_4OH.

\+100 ml 0.5 N H_2SO_4 (H^+ OK) xtrt 3 x 50 ml CH_2Cl_2

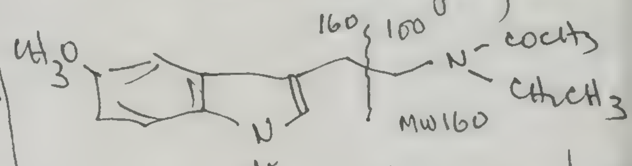
aq. ← pool CH_2Cl_2 x 100 ml H_2SO_4
← 3 x 50 ml CH_2Cl_2

pool evap (94B) . xtallizes! 0.44 g brownish

aq.
OH ē 6N NaOH (cloudy) flash
xtrt 3 x 25 ml CH_2Cl_2 0.80 g sharp
0.5 mm 80° no 0.45 g white oil swell.
110° no
160° no
190-200° yes.

IR
817
830
930
1109
1185

GCMS largely



vinyl = 173

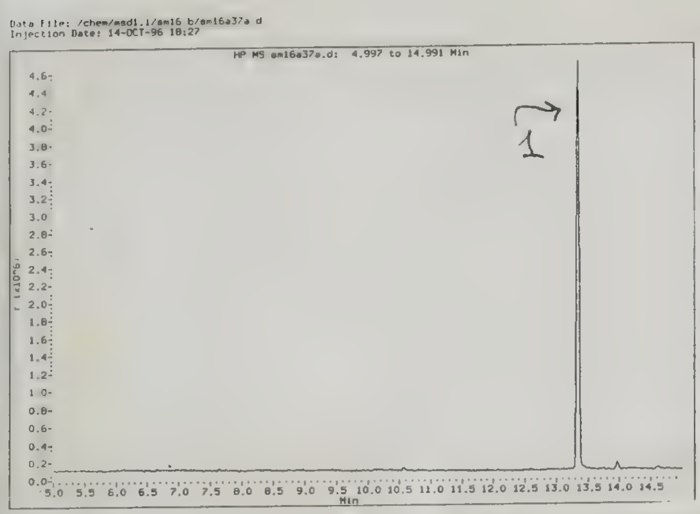
trace
melatonin = 232 MW

to page 101

.3 all into 2.5 ml IPA RT
\+ conc HCl (6 not enough dropwise 9 too much)
spont xtals start. slowly to final vol 20 ml ē anh. ether

→ 0.52 beautiful white xtals. calc 0.50 g 35%

Data File: /chem/msd1.1/sm16.b/sm16a37a.d
Injection Date: 14-OCT-96 18:27



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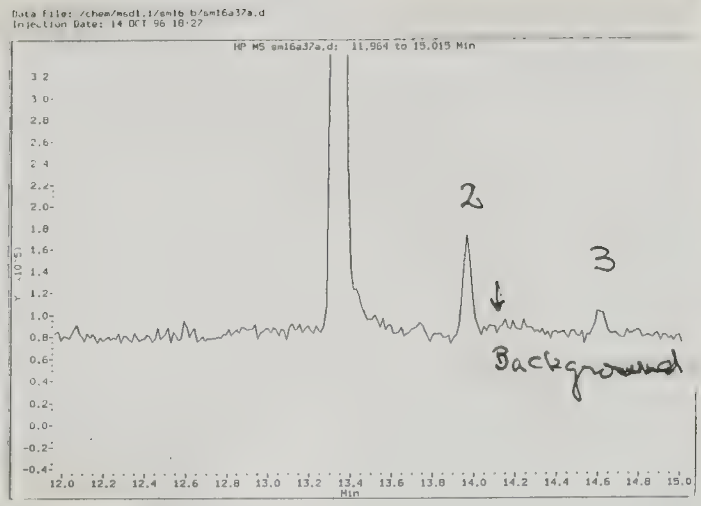
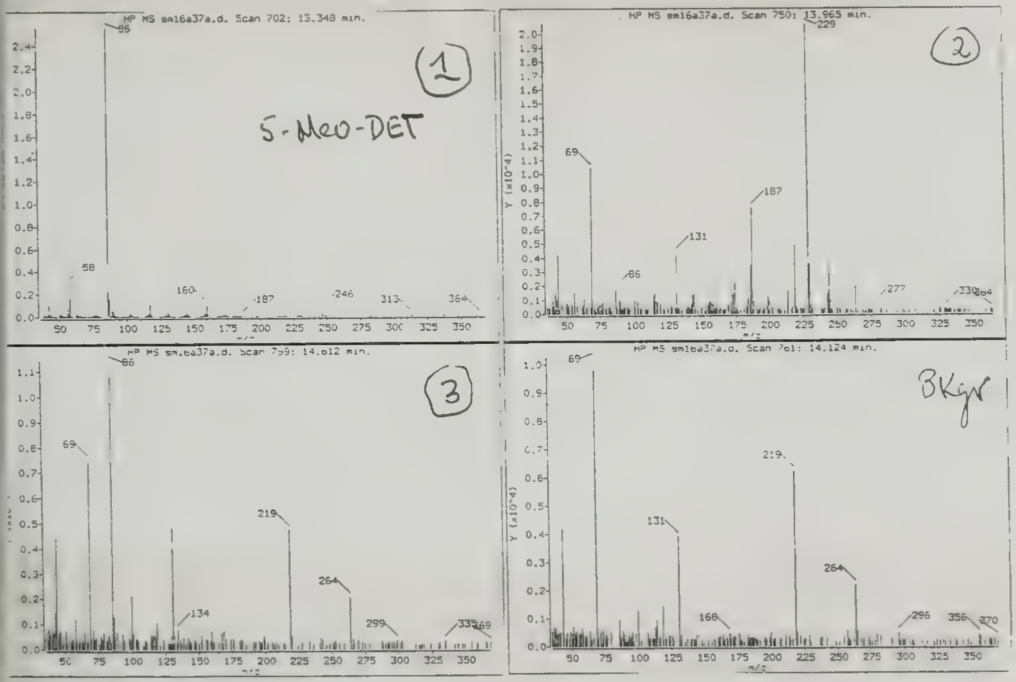
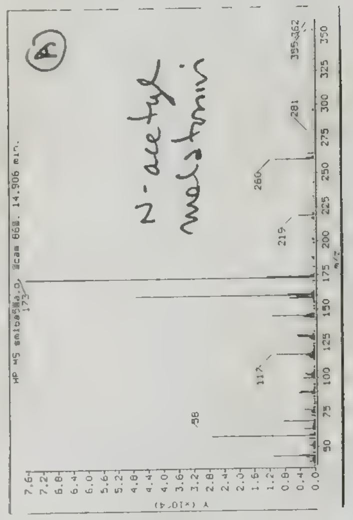
Injection Date: 14 OCT 96 18:27

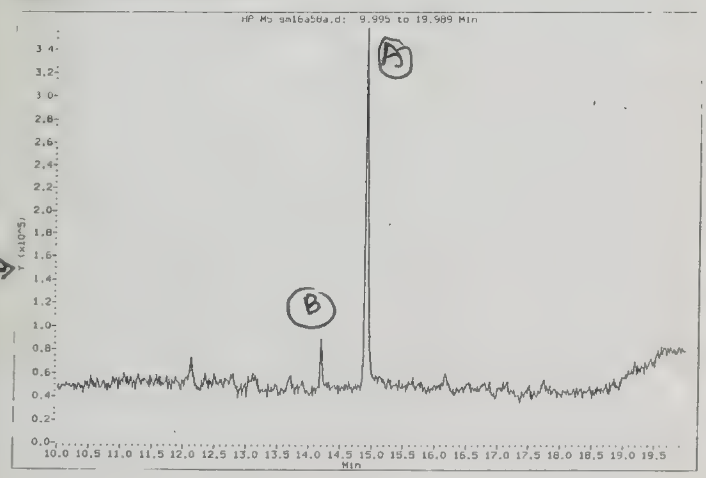


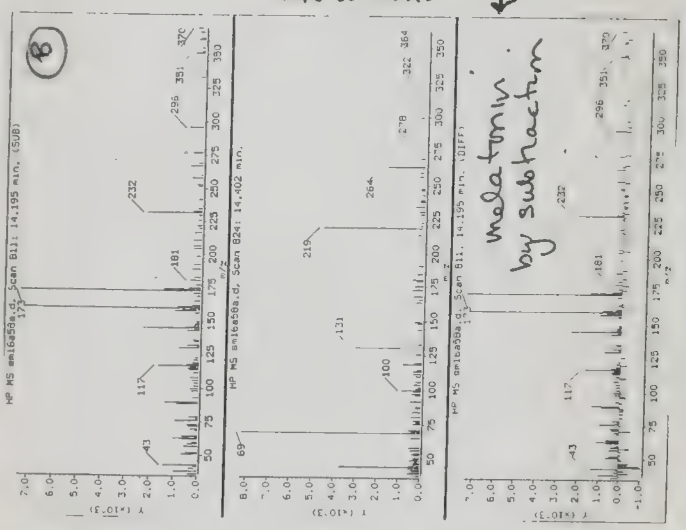




N-Et melatonin
melatonin

Data File: /chem/msd1.1/sm16.b/sm16a58a.d
Injection Date: 28-OCT-96 19:46

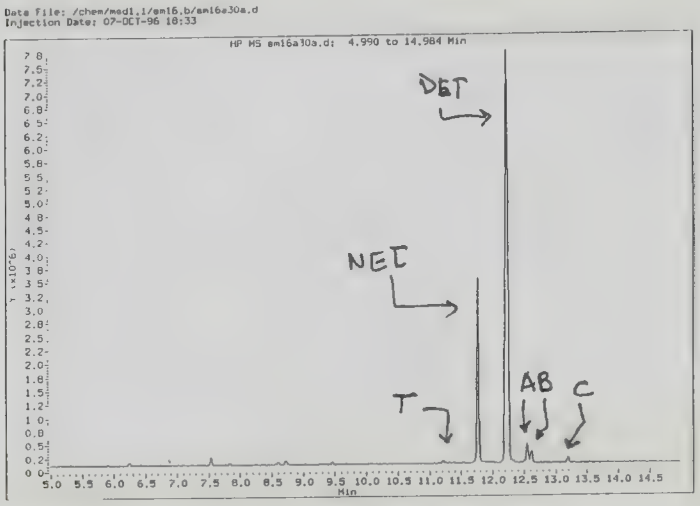




(96)

page 86 - preacetylation

Data File: /chem/msd1.i/sm16.b/sm16a30a.d
Injection Date: 07-OCT-96 18:33



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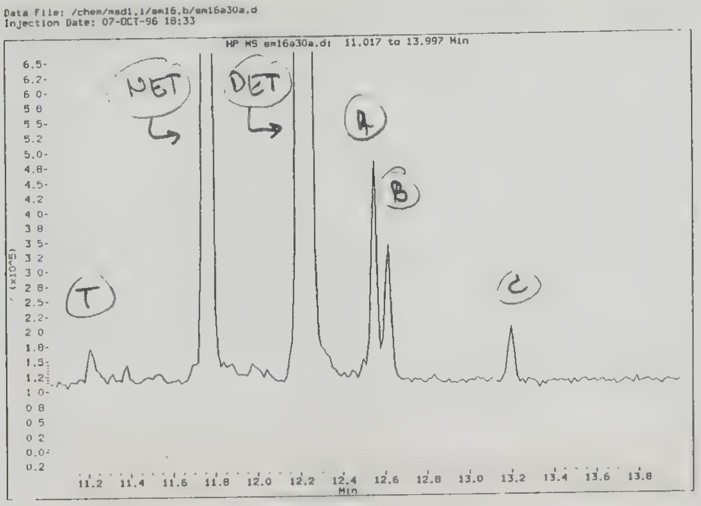
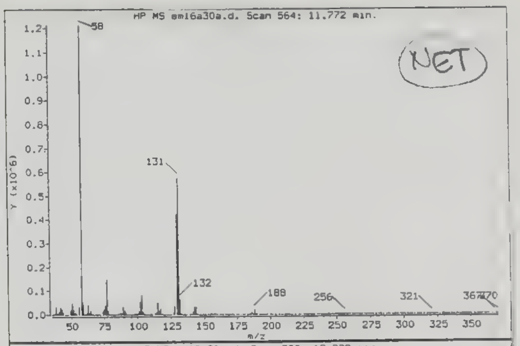
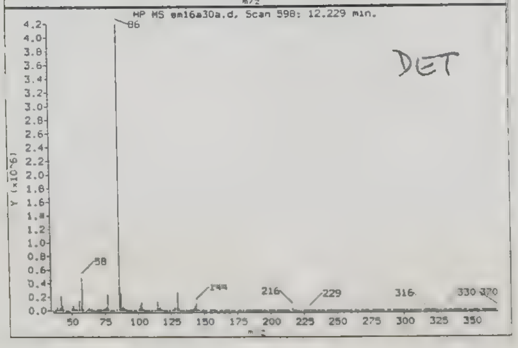
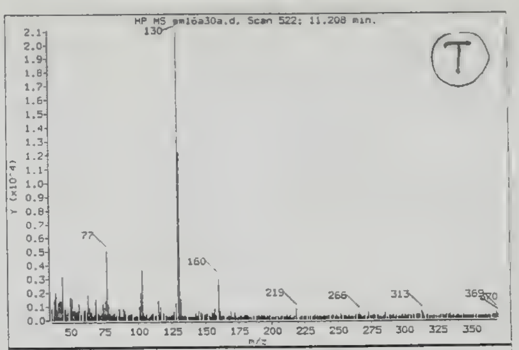
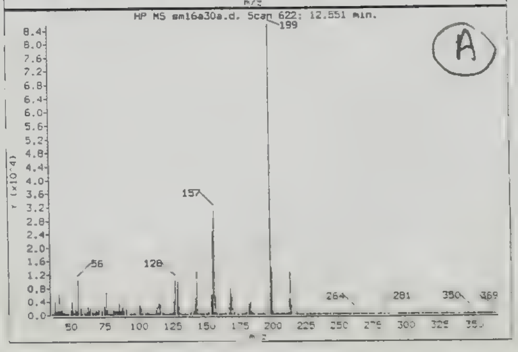
Injection Date: 07-OCT-96 18:33

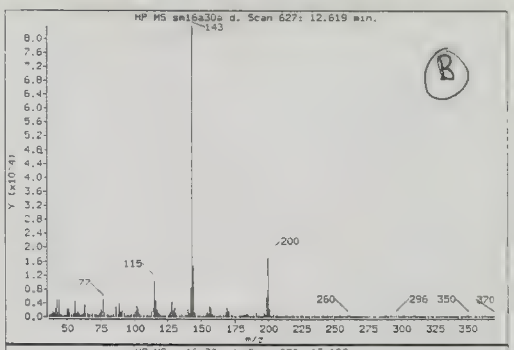


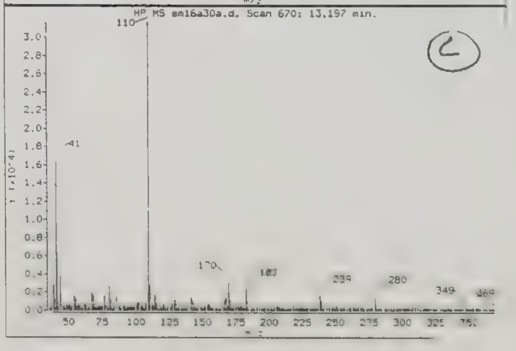






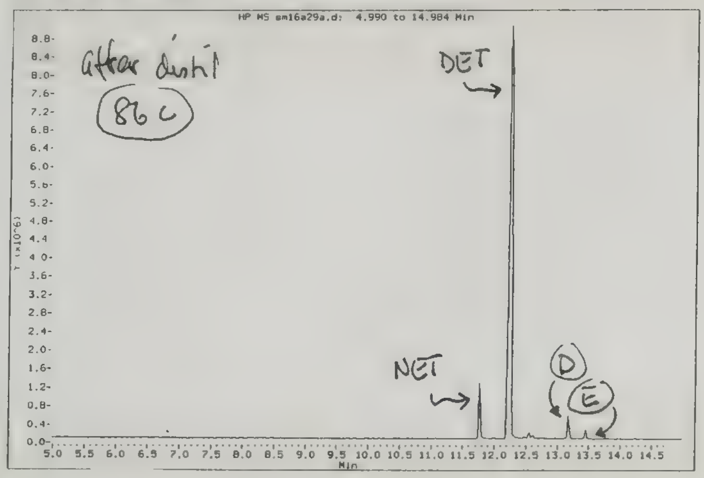






page 86 - post-acetylation.

Data File: /chem/msd1.i/T4747/T4747/sm16a29a.d
Injection Date: 07-OCT-96 18:12



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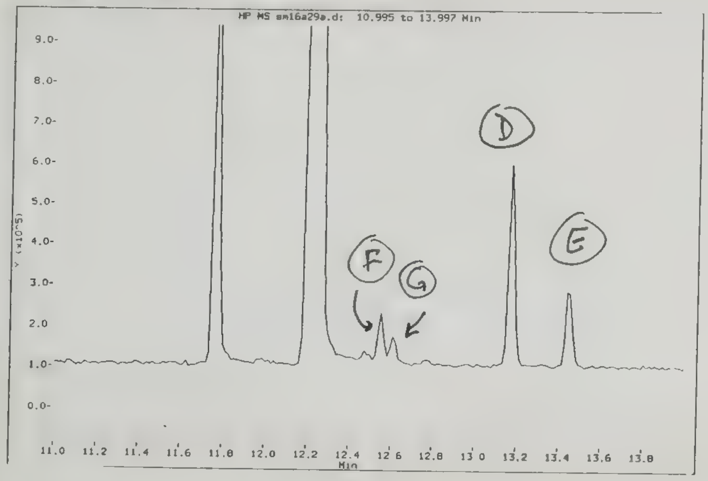
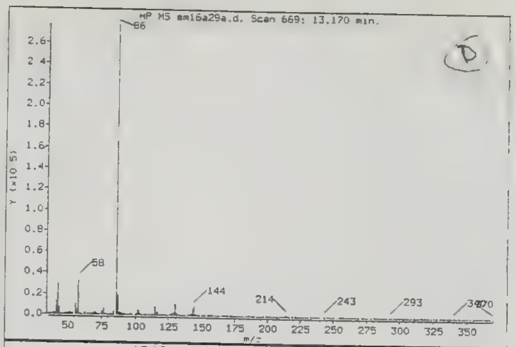
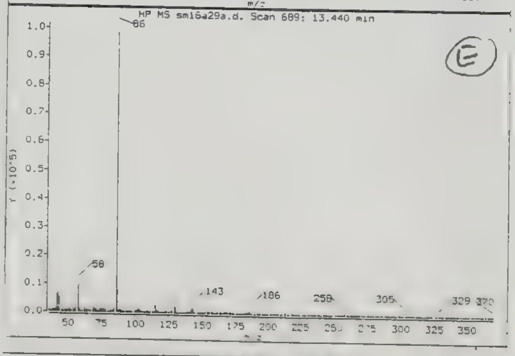
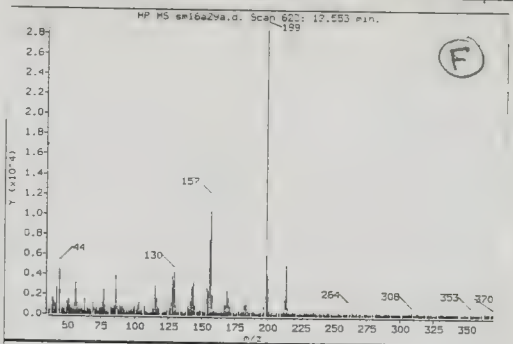
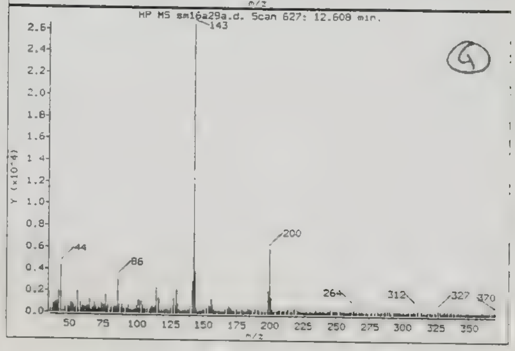




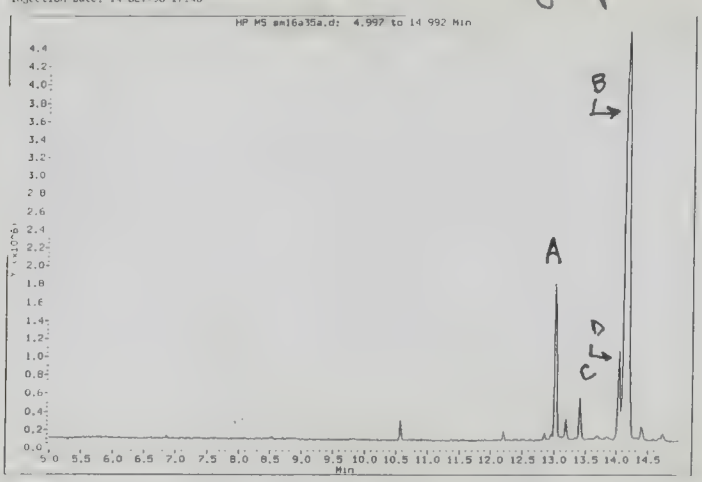


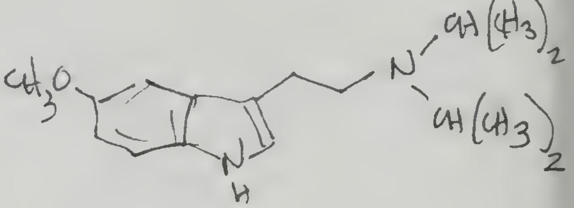


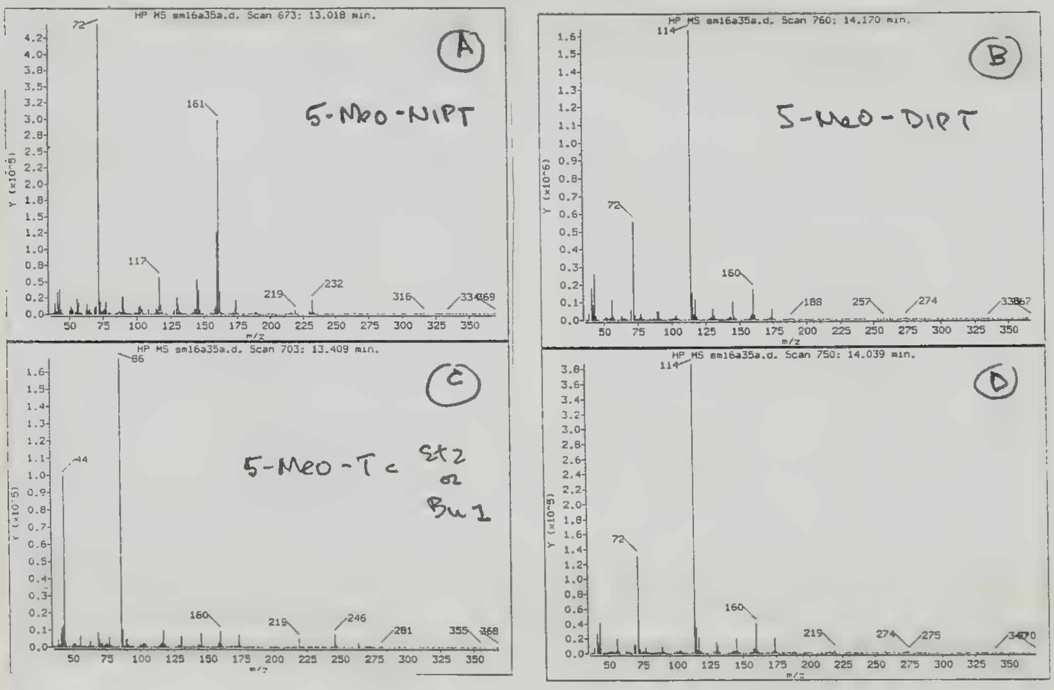


Spectra of purified 5-~~xxxx~~MeO-DIPT p92-3

Data file: /chem/msd1.i/sm16.b/sm16a35a.d
Injection Date: 14-OCT-96 17:48



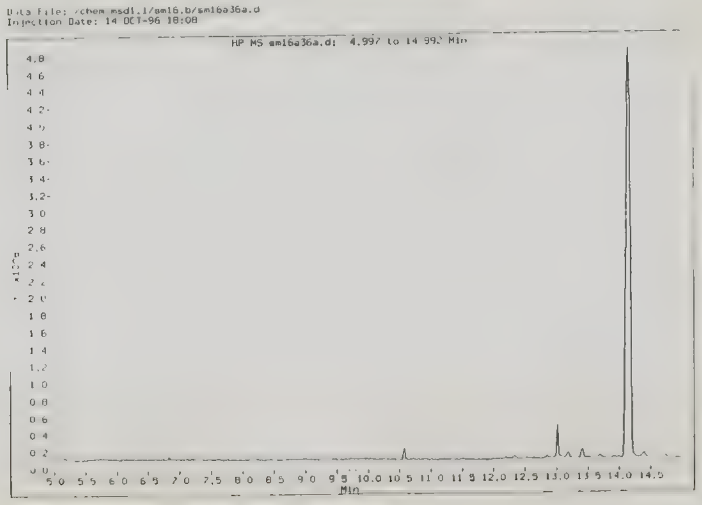


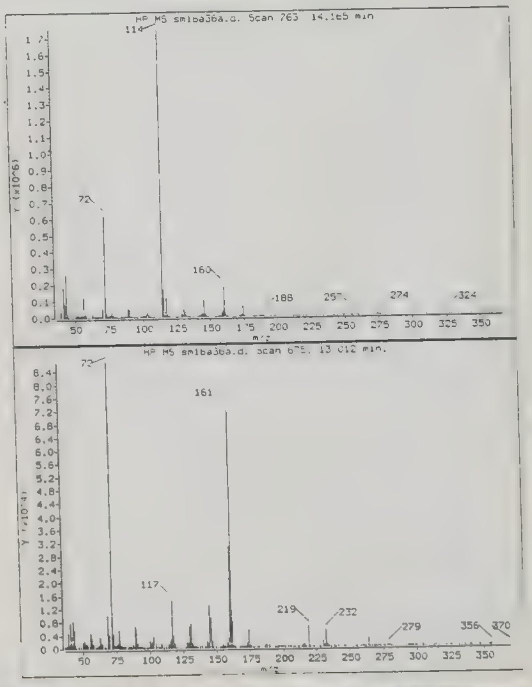


distilled oil

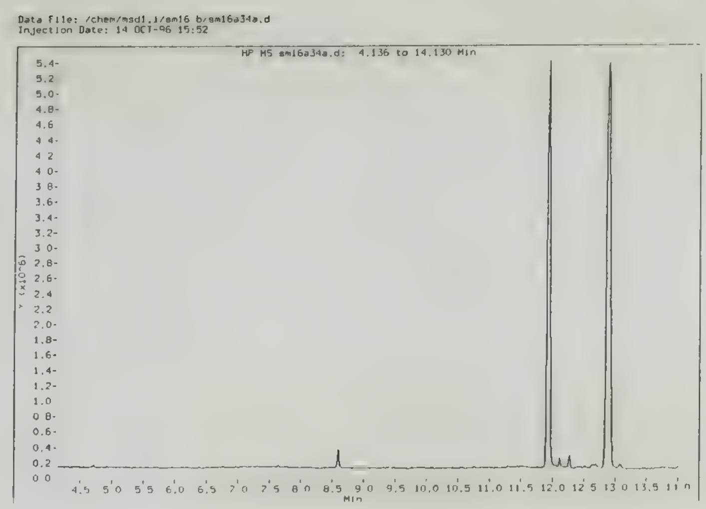
·HCl

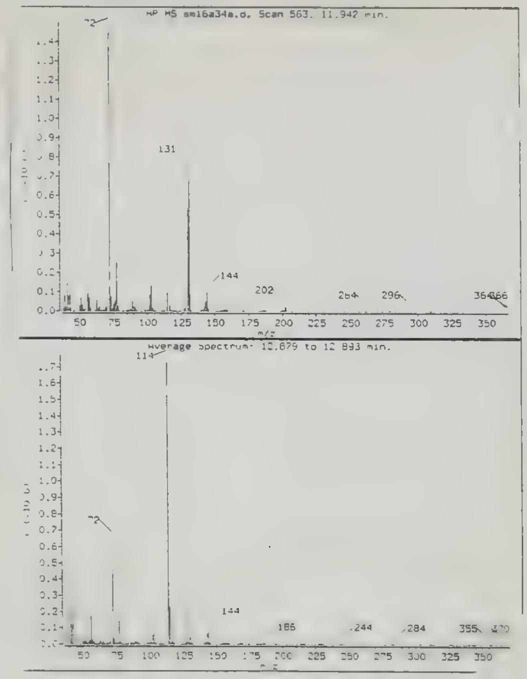
Data file: /chem/msd1.i/sm16.b/sm16a36a.d
Injection Date: 14 OCT-96 18:08





Work-up of page 89 - distilled, Ac₂O'ed DIPT



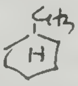


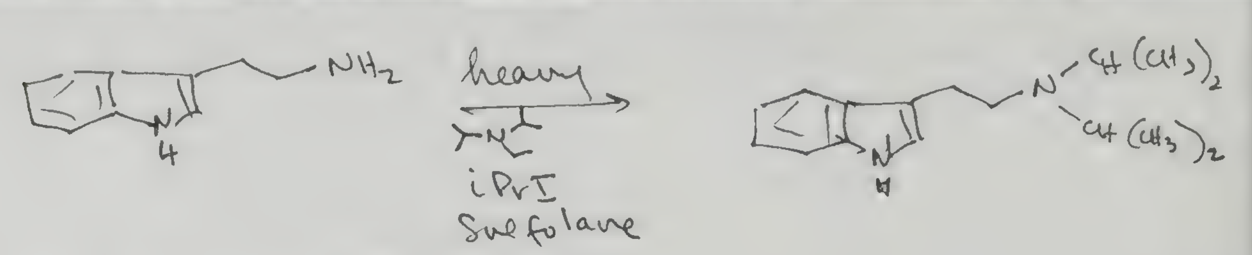
page 89
KR'ed oil → xtals. ~0.9g

grind under 10 ml Hexane —decant→ MLs pale yellow soln. evap → xtals 0.13g (89E) —wash c̄ sm amt hexane→ more xtals 0.02g (89F) ⟶ ML, to residual oil (a little xtal) 0.12g (89G)

↓

0.34g white xtals (89D)

Small amt ex  too soluble!
Small amt ex MeOH - too sol.
partition
MeOH / hexane



10 mM - use forcing conditions

1.6 g tryptamine
10 g melted sulfolane (not all dissolves)
6.5 g diisopropyl ethylamine
8.5 g isopropyliodide. 2 phases - shake occasionally
onto SB.

12 hrs later - darker, still 2 phases - off - into 100 ml - pH is blue, xtrt 3 x 30 ml hexane, pool - wash c 100 ml water - flash on R.E. → 2.67 g deep brownish fluid oil
ON → xtals under oil - decant

Smudge of fluid for GCMS (xtals in vial!) good spectrum - integrate by paper weight = 95.6% small amt NIPT - trace sulfolane, maybe not

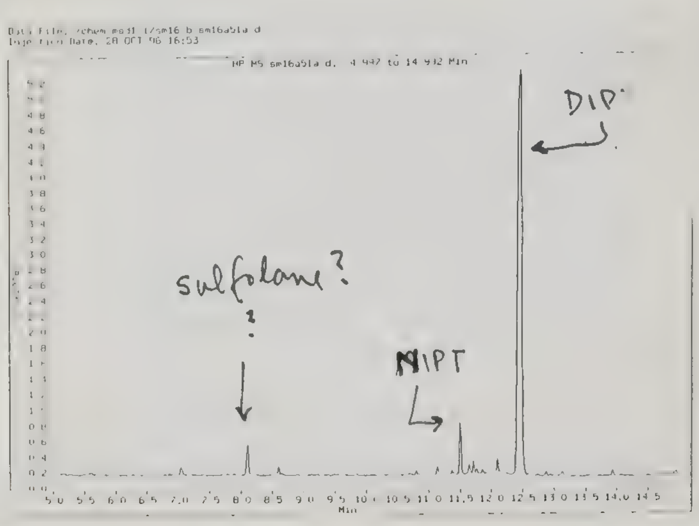
distill. 120° no
140° close
160° start
170° done

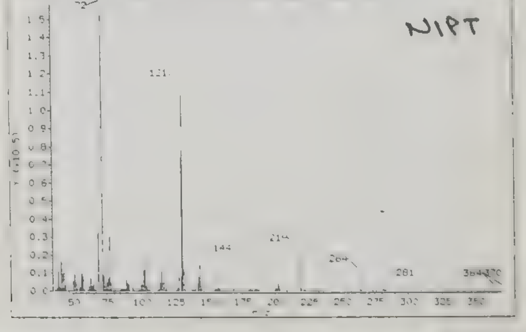
air evap. → 0.39 lt brown gummy ← crude combine → 1.034 dry.
↓
1.37 g 160-70° 0.05 mm
off white
mp 69-71°

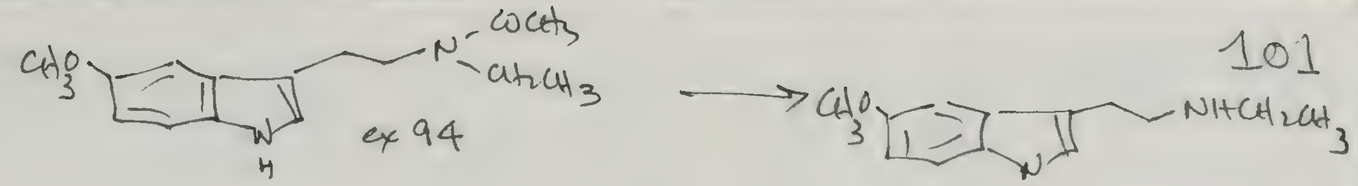
mp 72-74

recrystallize from hexane
white xtals MS gorgeous.
GCMS - free of sulf., NIPT totally!

1.37 g material - 0.50 g into 2.5 ml hot IPA, 9 drops HCl, 25 ml
c ether → 0.50 g B·HCl mp 192.5-193°







5-MeO-NET

0.44 g awfully good crude N-Et. melatonin from page 94

grind under a few ML MeOH → almost white solids - 340 mg. - Recryst a few milligrams from MeOH → white xtals.

some for mp
rest for IR
trace for TLC

0.30 g amide - 6 ml 5% NaOH - into SB. 2 hrs - still white solids - H_2O evaporating - + 3 ml 25% NaOH - Δ another hr. Still solids - no change - add ~2 ml IPA, looser - 2 hrs - going into sol. a couple of globs remain, keep at 100°.

IR. carbonyl: 1608 cm^{-1}

Fingerprint
790, 829, 929, 1031, 1068
1108, 1182, 1199.

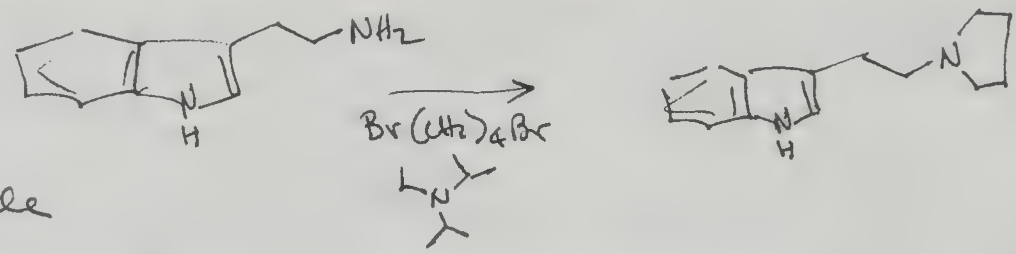
overnight - into 100 ml H_2O (is basic of course) xtrt 3 x 40 ml CH_2Cl_2 - pool - xtrt CH_2Cl_2 c 3 x 50 ml 1 N H_2SO_4

→ CH_2Cl_2 ±2g

flash → 0.24 g residue
film goes to solids
amide ?
when dry 0.19 g
almost white solids

→ aq.
wash c CH_2Cl_2
OH^- c 25% NaOH
xtrt c 3 x 50 ml CH_2Cl_2
flash
→ 0.05 g

(102) attempt



20 mM scale

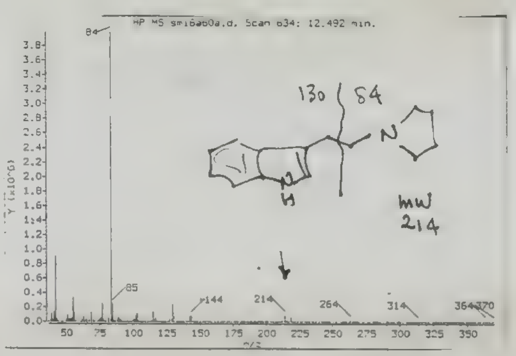
3.2 g tryptamine base, into 40 ml IPA, Δ to dissolve, add
7.7 g diisopropylethylamine 65 mM, add
9.3 g IC_4I 30 mM − Δ s/B overnight (RB, reflux.)
am − some darkened, solids on bottom, ∇ Rt → xtals
decant liquids   scrape out solids

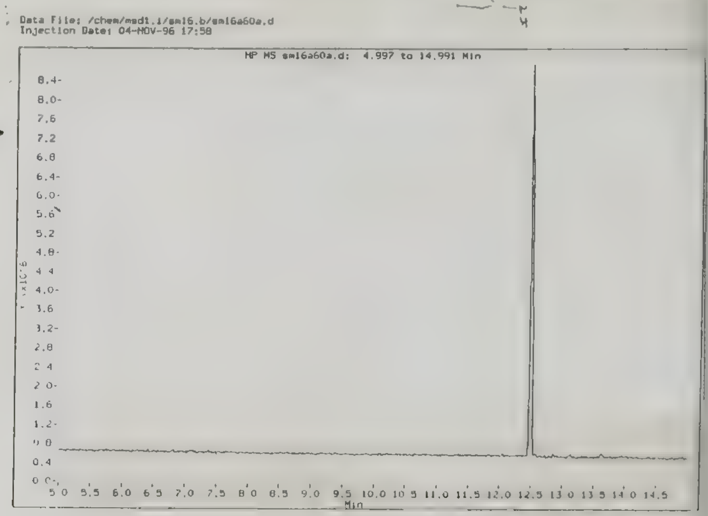
← flash   → 25.9 g dirty dark brown.

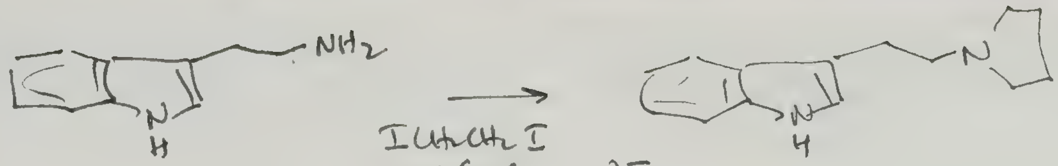
1.48 g tan solids
not sol Hexane
cloudy in H_2O

into 100 ml H_2O (neutral)
+ 25% NaOH · xtrt c̄ 3 × 50 ml
CH_2Cl_2 − pool + xtrt c̄ 3 × 75 ml
1 N. H_2SO_4 → color in the aq−
wash once with CH_2Cl_2
OH^- to pH > 9. xtrt 3 × 25 ml
CH_2Cl_2 − flash → 0.25 g. — 0.25 g / 0.25
KR 0.05 mm ~170−180° → white
oil that xtallizes − GCMS ↗
52 mg

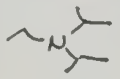
.05 mm
>110
145
start 170







ICH2CH2I
sulfolane RT.

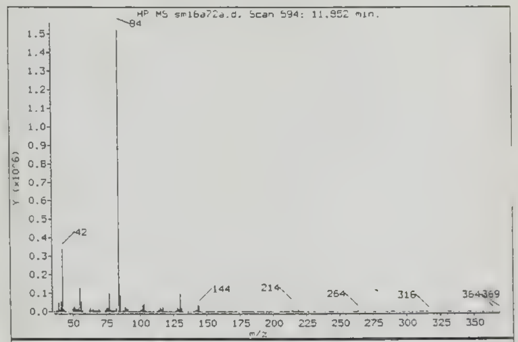
1.6 g Tryptamine base into 20 g sulfolane Δ a bit to dissolve
3.6 g $ICH_2CH_2CH_2CH_2I$ (10% xs)
2.8 g 

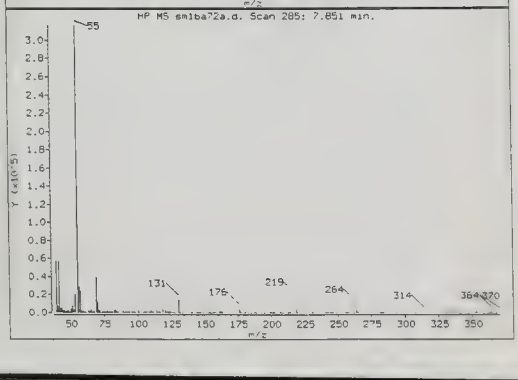
Stir RT - 15 hr work up - there is a 2-phase character to it all - into 100 ml H_2O (is basic) and xtrt c̄ 30 ml hexane. (there are globs not soluble in either phase). Strip hexane → 0.25 g stinky white

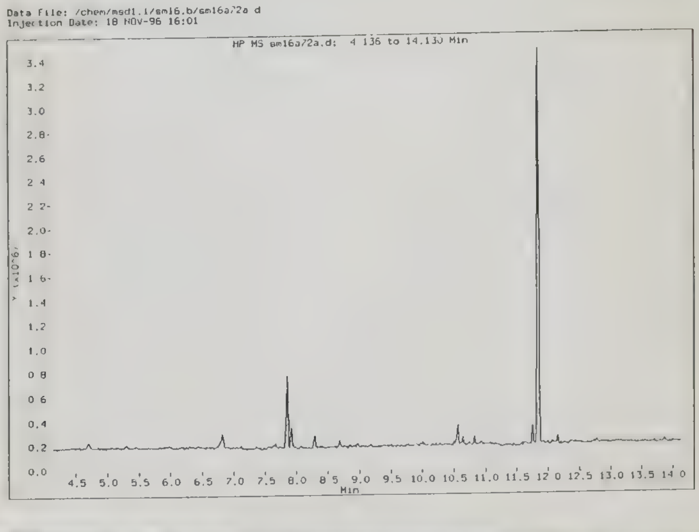
into ether for distil - strip down hard

↳ 0.08 g - distil → trace product

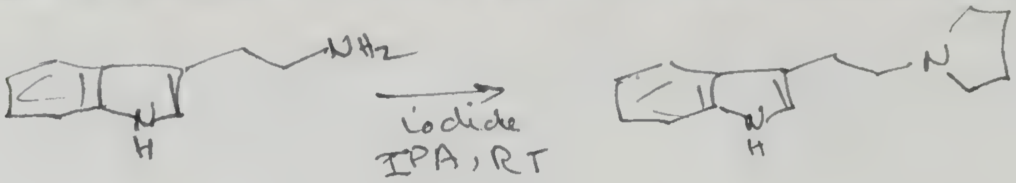
38.3 = 100% 84
2.6 7% 130
1.1 3% 214







(104)



1.6 g Tryptamine base into 20 mL IPA Δ ∇
3.6 g $ICH_2CH_2CH_2CH_2I$
2.8 g ~N~ stir RT a few days. Solvent evaporated
stand a couple of weeks.

(104A)

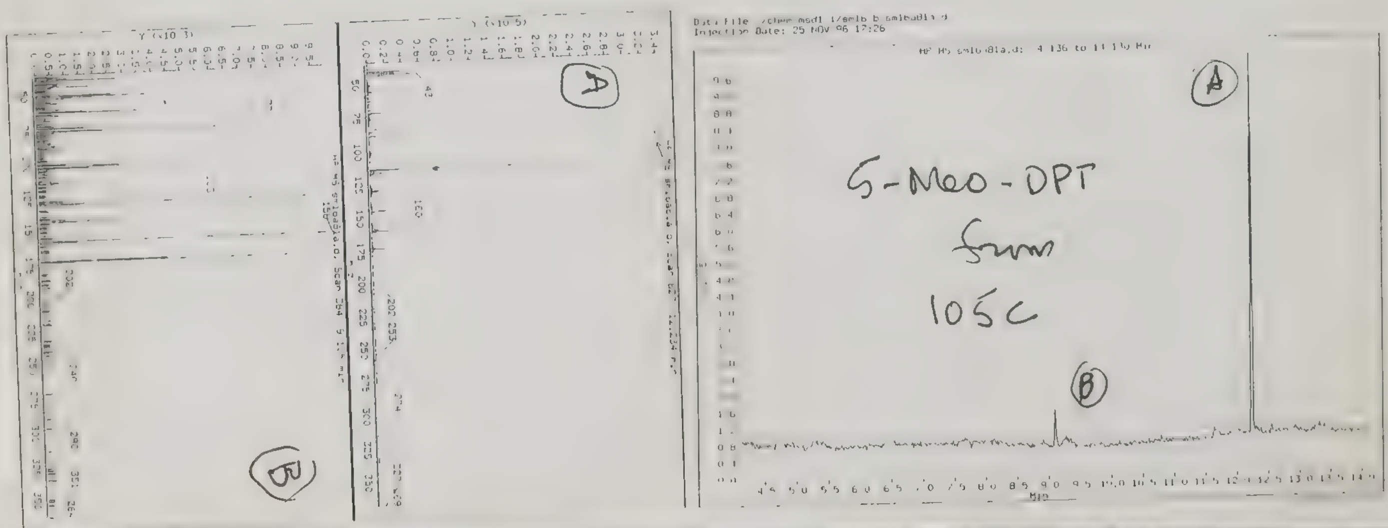
(1) aq. OH^-/hexane partition
hexane → ~.1g

(2) CH_2Cl_2 ginnd
filter, strip
→ 1.47. grand under hexane
flash. nil
under CH_2Cl_2 - flash
distil.

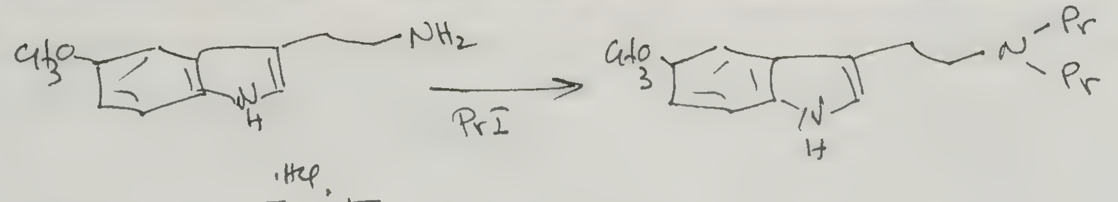
~160°
.3 mm
130 mg

I forgot I had started this so,
3.2 g T 30 mL IPA - not all in soln
9.5 g ~N~
9.9 g IC_4I stir RT
8 PM

(104B)

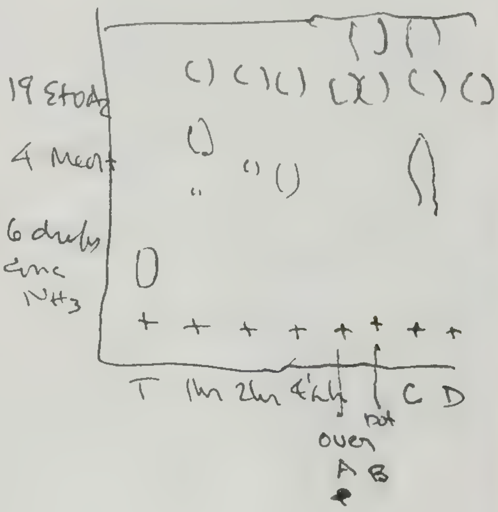


(105)



1.02 g 5-MeO-T ·HCl into ~ 50 mL H_2O, 5% base → blue pH -
xtrct c̄ 3 x 25 mL CH_2Cl_2 - flash → sudden xtals 0.89 g

0.89 g 5-MeO-T base in 10 mL IPA. Δ to dissolve - add:
2.8 mL (3:1)
1.5 mL $CH_3CH_2CH_2I$ very dark.
onto SB for 4½ hrs. (5 → 9:30 PM)
no T, mono & di - no quat



Strip on Rotary → smudge -
fair amt. modest smell.
add ~ 50 mL CH_2Cl_2 - absolutely
clear red-brown solution:
add 1 g Ac_2O. no Rx. boil on
SB for 5 minutes - stir.
add 2 mL aq. $MeNH_2$ - no Rx. stir.
add 60 mL 1.0 N H_2SO_4 - stays acid.
60 mL + 50 mL + 50 mL H_2SO_4 xtrcts
extraction.

CH_2Cl_2 red brown → colorless aq.

flash 1.79 g! (GCMS - 1 peak - 5-MeO-DPT bad background) ← (105C) (no amide seen) (don't believe it)

combine ← wash 40 mL CH_2Cl_2
flash → 0.51
stinks of amine

TLC product! (as sulfate)
partition between NaOH in MeOH
&
hexanes 4 x 25 mL
(all color left in MeOH) flash → 0.56 g pale yellow oil (105 D)
hexanes

.56
.54

to small 14/20 = 0.54 g

.1mm
160 no
.04
170!) 0.49
180!

KR
new vacuum tubing 170-180°/0.04.
beautiful white oil.
0.49 g,

into 2.5 mL IPA
7 too little 9 too much (drops HCl) slow xtal
+ ~25 mL ether - filter - ether wash air-dry
→ 0.54 g white! xtals IR fine mp. 193-194°

KR
0.103
120 no
150 no
up to 220°

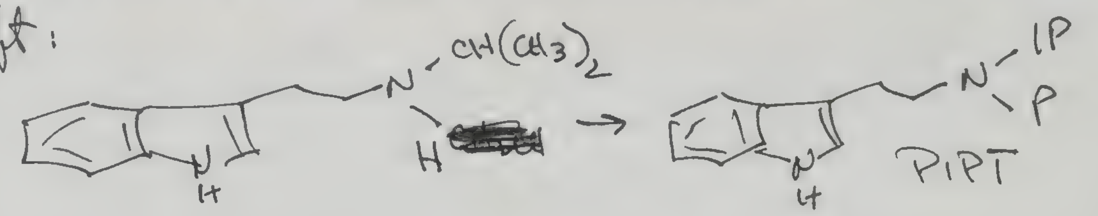
over
~0.01 g!
(105A)
one peak product!

pot
here in the rest
looks fine!
(105B)
one peak product

bad GCMS day.

(106) ~~Attempt~~:

MW NIPT	202
PrI	170
(amine)	129



0.50 g NIPT into 5 ml sulfolane - Δ SB to dissolve - won't - forgot it was the hydrochloride -

decrease - × 202/238

add 0.8 g 6N NaOH - then

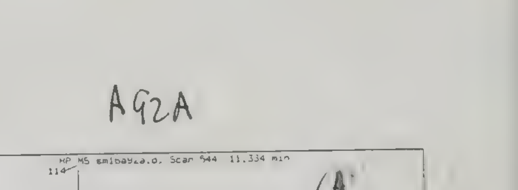
1.3 g (amine) (x2)

3.4 g (should be 1.7 for (x2) but some PrI may get ~~[struck]~~ chewed up ō the XS OH⁻)
PrI

Onto SB noon - off 5:30 PM - strip → black residue - add 100 ml H₂O - second error - it should have been MeOH - add 50 mL MeOH as well - now it is kinda in solution. Xtrt 3 x 30 ml hexane - flash

→ black oil 106A
0.14

~~[struck]~~ transfer, 0.10



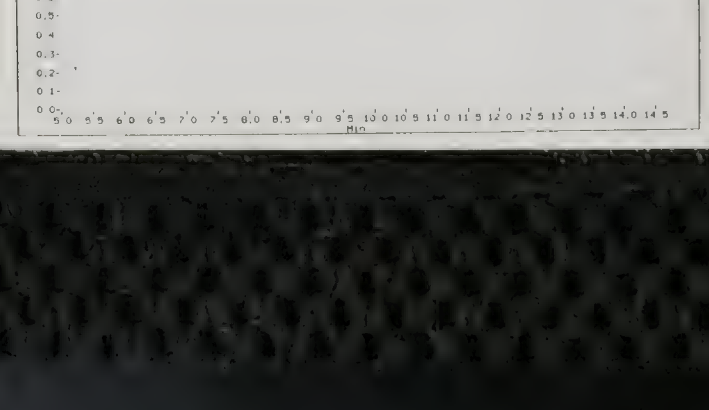
MW 244

130° haze no weight. OUT -
0.05 mm

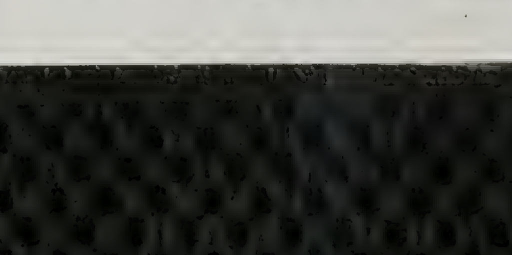
150-160° (guestamate)
0.05 mm Hg

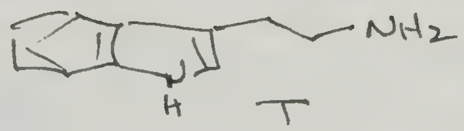
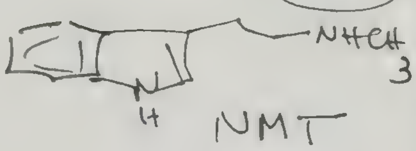
0.01 g - one droplet - save smudge for GCMS
PIPT. 106

GCMS - it is there - sensitivity of MS awful



A92A



Separate  T &  NMT

see 66

4.34 suspend in ~10 ml CH_2Cl_2

→ SOLIDS: solids 1.72 g, TLC largely T.

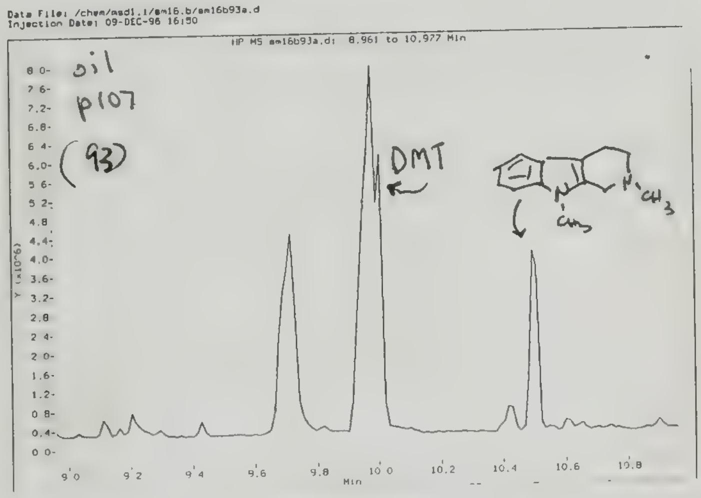
→ org. → OIL: flash, 1.82 g thick oil. TLC T, MeT, other stuff. (some dye slowly xtals?)

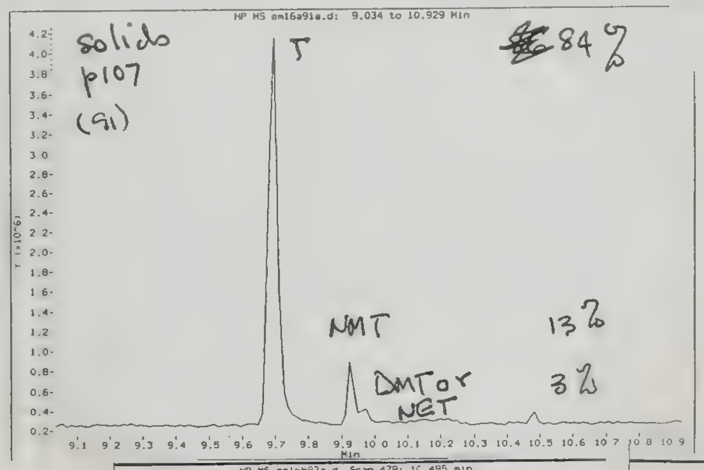
Solid	1.72
oil	1.82

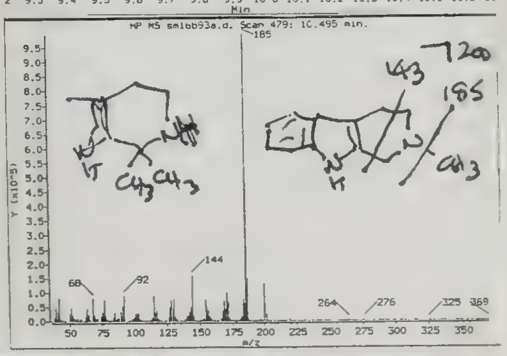
→ dissolve in 10 ml IPA. conc. HCl to red pH paper. scratch xtals (no seed no ether) 0.45 g. white solids

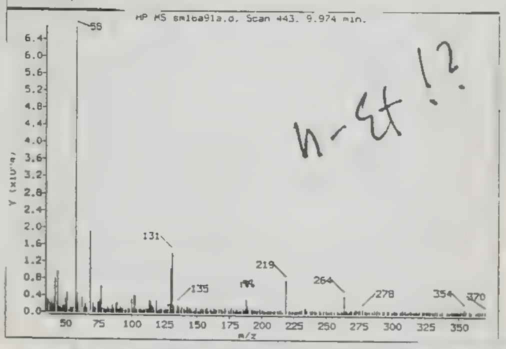
ML → + ~20 ml ether turbid. scratch - finally xtals, 0.19 g almost white solids

ML → lots of ether → oil; decant from → IPA ether decanting (signs of fine xtals on standing) → oil. residue



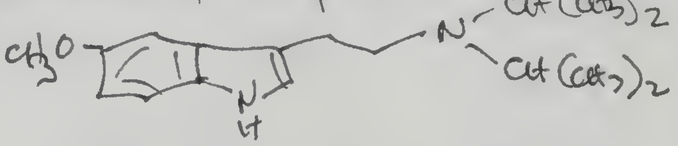






NO β-carb = 196

(108) Explore the neutrals from p 92



neutral fraction: strip hard on R.E. → ~~4~~ 4.60 g fluid liquid - to KR,

by 100° (0.05mm) big white fraction
4.00 g (sulfolane ?)
Sets to glass - yes!

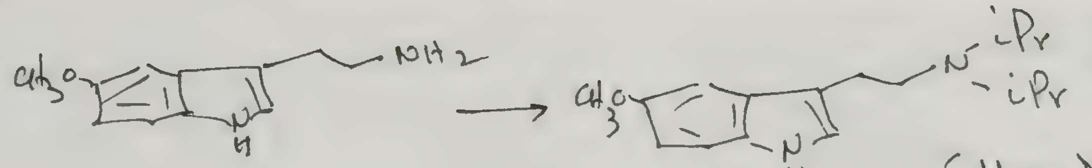
push by 170° (0.05mm) small, rather fluid fraction
~~[illegible]~~ g (sulfolane ?)
0.23 g.

explore briefly.
Save data for GCMS (108A)
hold for results. is sulfolane
no highers visible
but MS is not with much sensitivity

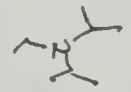
ir - out

Repeat.

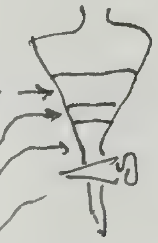
(109)



5-MeO-DIPT

3.0 g 5-MeO-T into
20 ml sulfolane. Δ on SB → clear soln. ∇ RT. add
8.2 g  4 equivalents. add
10.7 g colorless iPrI - 4 eq.s. Δ SB ~ 3 hrs - still
2 phases - stir at RT 16 hrs. Strip to fairly
thick residue on R.E. (30 g). add 100 ml H_2O →
clear solution !! maybe a wee bit basic ? add
a few ml 50% NaOH → very cloudy

Partition between aq. base & 3 × 40 ml hexane.
(extract with)



c̄ 2nd & 3rd extract - more
colorless hexane could be giggled out
of the deep brown interface

clear hexane xts pooled - stripped → 1.76 g almost
white oil - stinks of amine.

Transfer to 14/20 RT - c̄ a bit of CH_2Cl_2 - really strip on
R.E. → 0.99 g pale cream-colored oil - slight amine
smell. To KR. fogging over at 100° (0.01 mm!)

↳ trace (109 A)
(very fluid) (10 mg)

beautiful white oil over
at 140-150° (109 B)
0.80 g

no residue!

0.05 mm
90° no
100° lite. fogging
flame out to 2nd trap.
140° white oil over!
150°. some still in pot
0.80 g. white

dissolve into 3.5 ml IPA
conc HCl (<25?) 10 to 15 yes.

no xtals. add 5 drops ether - xtals start ✓ - another 10 drops
scratch

10 minutes filter - wash c̄ 4/1 IPA/ether - air dry

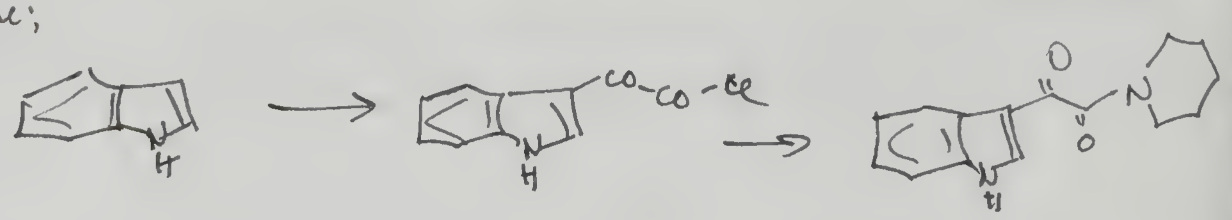
beautiful xtals white (109 C)
~0.85 g.

(ML S evap 109 D)

mp. 181-182°

MS 114 100% CH_2N <(iP)(iP)
~30% 72
~10% 160 trivial parent

(110) Explore;



towards pip-T

1.0 g indole in 15 ml TBME (solution) – to this, add (over 30 min, was ∆ at 0°?)

1.1 g oxalyl chloride in 15 ml TBME.

stir another 15 min, filter solids, wash briefly c̄ cold TBME. – add, c̄ stirring, a bit at a time, to

2.0 ml piperidine neat. Add xs 2.0 N HCl → solids – filter. air dry. 1.29 air dry mp 175-178°

recrystallize f. 7 ml hot MeOH, filter, wash lightly, air dry → 1.01 g white xtals. mp 182-183°C

cot.

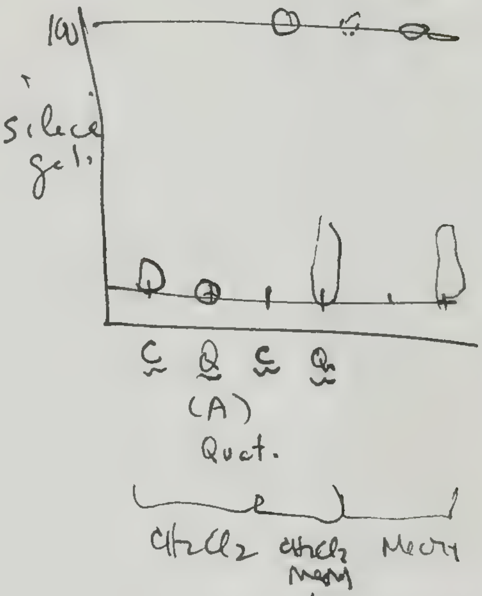
Cotenine quat.

0.25 g C PU 5 41 add
10 ml CH_2Cl_2 – add
0.50 g CH_3I – stir awhile – overnight – Am – flask – heavy oil. wash c $CH_3CH_2OCH_2CH_3$ → slight oily ex hate – still dark brown oil (A)

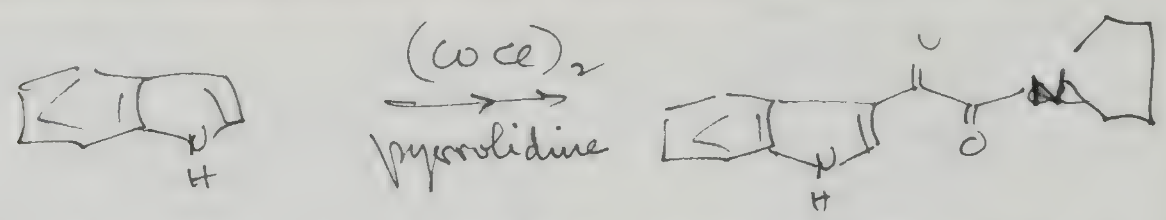
half to vial

half still in flask

into 1/2 ml H_2O
xnt 2x Et_2O
flash ag.
↳ dark oily spots.



MeOH + 10% NH_4OH no different.
Quat irreversably bound to Silica

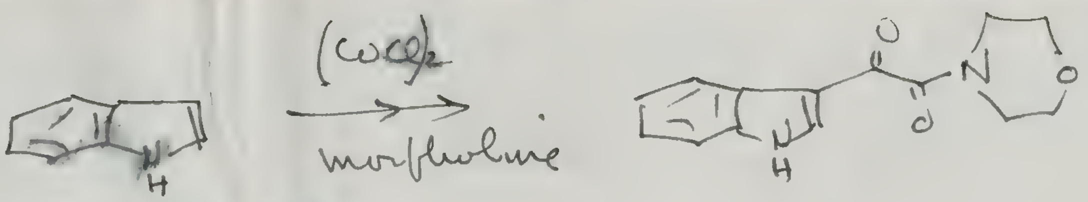


A solution of 1.0 g indole base in 15 ml TBME is stirred well. There is added, dropwise, a solution of 1.1 g ClCOCOCl (theo 1.17 g) over 20 minutes (solids appear at 1/2 addition point) stir an addn 10 min. Filter → yellow xtals – wash sparingly c̄ RT TBME – add as a solid, a "bit here" at a time to stirred 2.1 g pyrrolidine neat. Exothermic, → white solids & color in soln – when RT, add 80 ml 1N HCl. stir pink filter, wash c̄ H_2O → 1.62 g wet off-white xtals. yellow -15h.

at not quite dry weight of 1.2 g – try 10 solvents for rextal – too insoluble MeOH IPA TBME toluene, EtOAc etc. CH_3CN Perfect.

dissolve all in 30 mL boiling CH_3CN – slow to dissolve – ∇ RT white xtals – color in ML!. (most) slightly off white, fine xtals. filter, wash lightly c̄ CH_3CN – air dry white xtals dry weight 0.87 g

mp 219-220°



≡ to page 112 down to "here"

here - added to 2.0 mLs morpholine - stirred - exotherm - but stays large white. let cool - then add 80 ml 1 N HCl. filter, wash c̄ H2O - remove, grind up the chunks under fresh water filter → white xtals 1.55 g wet
let partly ~~air~~ air-dry.
0.95 when completely dry.
pale pink.

recrystallize from 4 ml MeOH at the boil - filter - wash extremely sparingly with MeOH - air dry to
.75 of 4ml — constant weight - white 0.75 g - crude mp 183-186
ex MeOH → mp 187-188°

MET
Tryptamine, N-ethyl-N-methyl
Indole, 3-[2-(ethylmethylamino)ethyl]
N-Ethyl-N-methyltryptamine
3-[2-(Ethylmethylamino)ethyl]indole

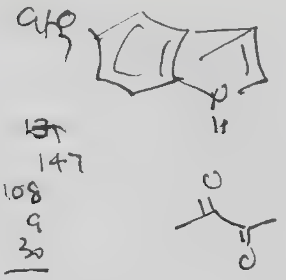
See under MIPT

SYNTHESIS: Under an inert atmosphere, a solution of 7.0 g N-formyltryptamine (see preparation under the recipe for N-methyltryptamine, NMT) in 50 mL anhydrous THF was added to a well stirred mixture of 7.0 g LAH in 100 mL THF. This was brought to reflux temperature, and held there for 3 h. There was then added 11 mL EtOAc at a drop-wise rate, and the mixture held at reflux for an additional 2 h.

work-up same

The reaction mixture was cooled, and diluted with 70 mL Et2O. The excess hydride was destroyed by the addition of 7 mL H2O, followed by 14 mL of 15% aqueous NaOH, ~~10 g Na2SO4 and 10 g MgSO4~~. After an additional 15 min stirring, the mixture was filered, the inorganic solids washed with Et2O, and the combined filtrate and washes were stripped of solvent under vacuum. The residual oil was dissolved in a small amount of anhydrous Et2O

Et_2NH
73



~~137~~
147
108
9
30

147 → 274 → 246, 282.5

1.5g → " 2.80" → 2.1 → "1.89 " 2.17"

80% = 2.24g

1.89 2.17

742 → 1.40
1.60

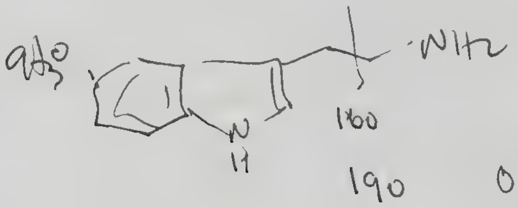
246 0.45
↓ ↓
282-5 51.6 " "

·HCl

160
86
246
36.5
282.5

.45g 145
2.5 ml 8ml
~~142~~
IPA

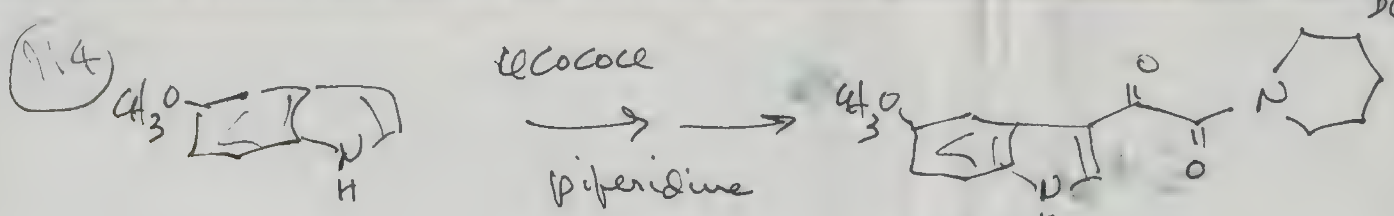
50g



160
190 0.95
↓ ↓
282-5 " " 1.41g 0.50 g z

[illegible] .40 .60 [illegible].45 [illegible] 5.6 5.5[illegible]

(7.14) DONE



a solution of 1.25 g 5-MeO-indole in 15 ml TBME was stirred, and a solution of 1.1 g oxalyl chloride in 15 ml TBME added over ~~...~~ 20 min dropwise - 10 min tomato-red xtals start to appear, ~~...~~ stir another 10 min, filter. - wash with a little TBME - loose "hn" tomato xtals - add a bit at a time to 2 ml piperidine - stirred - exotherm & fume, of course. end up adding ~1 ml more piperidine to get everything wet & all tomato gone. to RT - + 80 ml 1N HCl - gunky - stir for quite a while* - dig out gunk - get most of the water off by Kleenex dabbing - grind ~~...~~ under MeOH ~2 ml? solids - filter →

0.82 g cream xtals

mp 153-158 → 0.65 g totally dry.

recrys f. 2 g MeOH in hot. out (seed) ▽. → 0.37 pale cream fine xtals mp 167-169°

← aqueous, filtr → 0.01 g pink solids out

---

page (115) continued - filter → wet cream colored solids - dry in SB 100° → 1.13 g cream colored powder

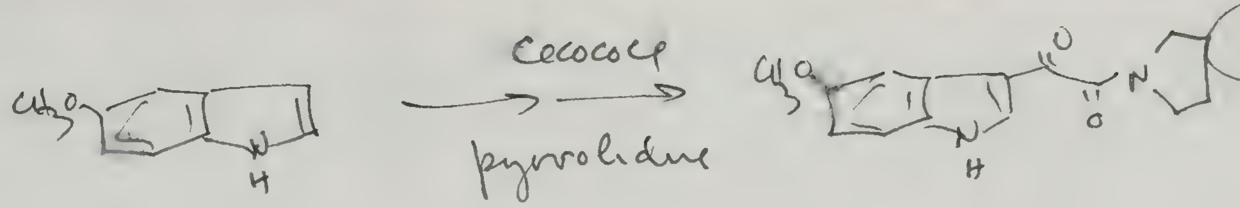
Sample for MP 115B crude. mp 180-~~200~~ 195 area!

Recrystallize from 15 ml boiling MeOH (decant from a wee bit of (insoluble)) clear hot - ▽ RT → xtals, filter → white solids, xtals - amber ML

↳ air dry. pale cream .75 wet c MeOH. .65 dry.

insoluble - wash c acetone - air dry. 'white'. mp 211-212 ← IR's identical → mp 210-211

(acetone insoluble!)



Identical to ← to "here"

deep tomato color — 30 min + 15 min
deeper than 114

"here" make a mix 2.1 ml pyrrolidine & 2.1 ml (diisopropylethylamine) – stir well – add deep tomato xtals a bit at a time pasty again – add 10 ml water first – then some 1 N HCl – some solids – much gum. – filter all out (solids, gum) grind under 3 + 1 ml MeOH –

.39 wet — filter → creamy solids – grown up particulate – no clean crystals – save for mp. into 2 ~~ml~~ g (2 1/2 ml) MeOH – Δ SB → soln – ▽ to rt → white xtals. filter – .36 g product.

.82 g MeOH

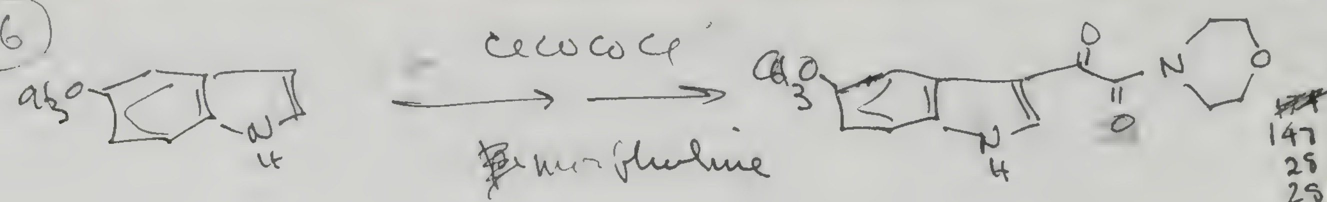
.48 wet rextal. — brownish product 0.16 g. xtal a bit from MeOH – not good loose

gum sets up solid 0.15 g grind — brown to olive green solid — ugh. (nothing) — gives olive colored solid, 115A. OUT all.

Repeat – drop innovations same scale 1.25 indole (15 ml TBME) 1.1 g oxalyl chloride (15 ml) – dropwise over 20 min – 10 min stir – normal not dark tomato solids. filter wash brief air dry – add dab by dab to 2.0 ml neat pyrrolidine. This time rubbed all the cake into ~~the~~ the basic mush – all finally decolorizes to cream color – and it sets up to a sorta solid (15 min of rub – keep homogeneous – good pastiness – add 20 ml 1. N HCl → nice solids – rub the chunkies c̄ a spatula until all fine

(116)

MW 289



147
28
28
14
28
28
16
289

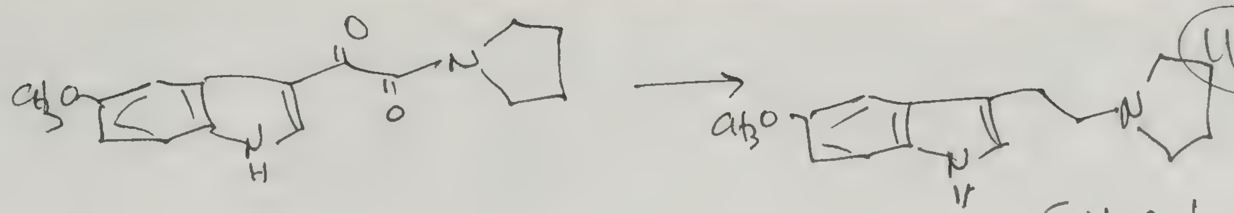
usual combo:

1.25 g 5-MeO indole in 15 ml TBME, stir, add
1.1 g ClCOCOCl in 15 ml TBME over 20 min - Solids
at about 5 min. Really over this period, and got a normal tomato xtal - not dark tomato. Stir another 10 min - filter, wash c̄ TBME, air dry (briefly) & add dab wise to 2.0 ml neat morpholine. Take time making it all homogeneous (15 min) until all tomato is dispersed in the oily fluid - becomes dull reddish brown. Then add 80 ml 1N HCl → solids - grind up the chunks - no gum! - filter, wash c̄ H2O - onto SB at 100° → dry powder - rust red - 1.35 g

Small amt - out of MeOH OK. costly.

All 1.35 g amide in 10 ml MeOH Δ SB → clear blood red solution - ▽ → xtals. wash sparingly c̄ MeOH → white - blood red ML → let evaporate

Solids -
0.85 g - very wasteful.
tinge of pink color mp 193-194°



5-MeO-pyr-T

25 mL 1 N LAH in THF (cloudy) in a RB (300 mL) under Argon - Δ to reflux c̄ stirring - add dropwise over ~20 min 0.65 g 5-MeO-pyr-amide in 25 ml dry THF (heated a bit under Ar to dissolve. mostly stays in. Exothermic rx c̄ each drop. Hold at reflux 48 hrs! ∇ to RT - Kill c̄ 50% aq. THF - reasonably loose Al_2O_3 - vacuum filter through paper - wash c̄ THF. oxide goes to a unfiltrable gel.) ML — to residue on rotary → goodly amt

7 ml 50%

gel - break up under water

1.39 g

of almost colorless, fluid oil. Reasonably OK smell. Then, while still slightly warm it vigorously decomposed (!?) with the evolution of some gas & the development of a dark black area. still fluid, but now deeply colored - into CH_2Cl_2, xtrt 3× N HCl

110 mg.

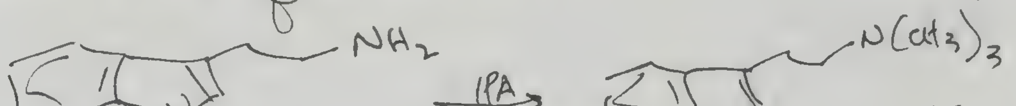
~8 ml IPA, 14 drops ether → 2 crops HCl

CH_2Cl_2
wash c̄ bicarb.
flash → deep brown oil
~300 mg, TLC - no product?
distill anyway.

↓ aq.
OH - cloudy
xtrt CH_2Cl_2
flash
→ 100 mg
thin, almost glass
GCMS terrible

no N fragment

(118) explore IPA as quat solvent.



based on reasonably insoluble IPA wash @ page 69.

3 g T - into ~~30~~ 30 ml IPA (Δ to dissolve, stays in at RT.) - add (stirring) 10 g MeI. - no exotherm. 4PM Thursday. First xsols in 10 min. no exotherm - 1 hr - heavy c̄ solids (stirrer stopped - too thick)

~~@~~ In AM. - filter → cream colored solids - 2.72 g wet
wash c̄ IPA →

mp
as is 175°

Xtal H2O 203-4°

wash hot IPA 192-4

Xtals CH3CN 210-11

dry 1.81 g

into Tihkal

Repeat 115 - Surfer → dark product ē cocc in R_2OH - HCl ↑ .96 ← 2.13 dark
dry. wet

Repeat 115 - we 1.25 mdole 15 MTBE
1.05 cecococe (inadequate) (fresh) 15 MTBE
2.0 ml pyrrolidine

differences, first cecococe, from Acros.

3.42 wet

3 ml acetone

1.42 (wet)

.97 air dry.

addn - 20 min → light tomato - stir 15 min - filter - wash (by suspension) in TBME (RT). Air dry several min. to rather loose xtals. Add (scatter, not bunch-wise) to 2.0 mL pyrrolidine. The few dark spots rubbed in ō spatula → dark cream viscous oil. Add some 1N HCl → off-white solids - grind up chunks, filter, wash ē H_2O → 3.42 g wet solids

grind under 3 ml acetone to almost white paste - it seems to firm as I work with it - Filter - wash ē very small amt. acetone. → 1.42 wet. ON air dry 0.97 g 0.94 ē xtal removals

0.94 g into 12 mL boiling CH_3CN - clear, ∇ to RT let stand ~ 1 hr. filter, wash sparingly ē CH_3CN → 0.72 g wet

0.69 g dry

mp 212-213°.

used most p 120

(120) Retry page 117.

5-MeO-pyr-T

25 ml 1N LiAlH4 in THF stir, under Ar.
Δ to boil add

.67
− .23 mtSM
.44

0.44 g 119 dicarbonyl in 25 ml dry THF

add in ~ noon. reflux ON. AM. ∇ RT − add wet 50/50 THF until no H2↑, then 5% NaOH until curdy. filter wash c̄ 50 50 THF. strip − into H2O (basic OK) xtrt c̄ hexane (60 mg) xtrt c̄ CH2Cl2 → 0.37 g − combine distil

↳ 110 mg viscous pale amber oil
MS see below

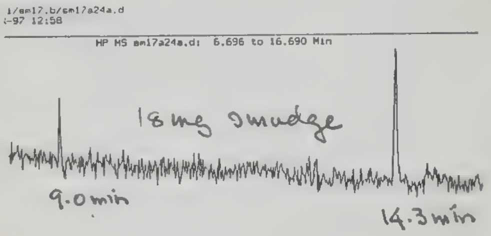
60 mg hexane xtrt

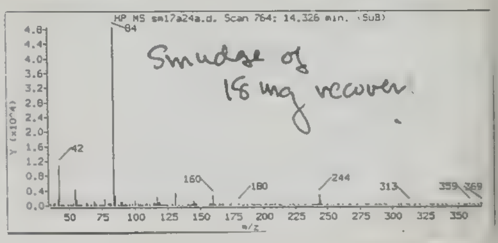
CH2Cl2 .37 g

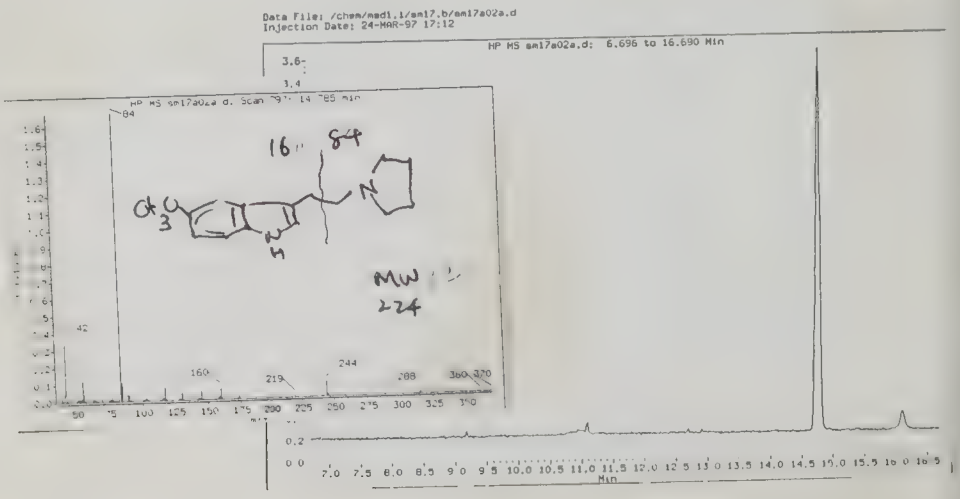
combine

~ .05 mm
40 over
100 gone again
120
160 clouding
170 0.04 mm
110 mg. no xtals
into .6 ml IPA
HCl (2 drops)
ether → oil.
strip → black oil

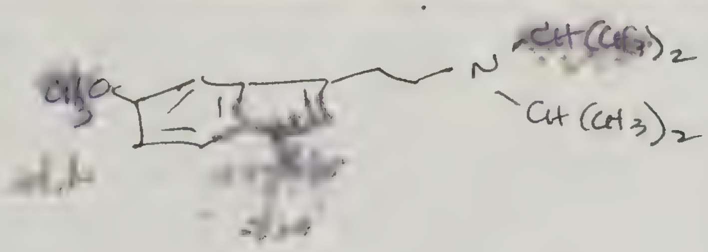
try to make .HCl − black oil − stand scratch nothing works − into 1 ml H2O (not completely clear) + 5% NaOH → very cloudy − xtrt CH2Cl2
flash → 30 mg − try KR 0.03 mm/Hg. 140 blush take to 200° → 18 mg film







~~[illegible]~~. see 109



2.07 g 5-MeOT
.15 ml sulfolane Δ SB → sol'n ∇ RT
5.5 g [structure]
7.2 g iPrI (goofed, used 7.9 g, sorry)

SB 6 hrs. darkens quite a bit - looks almost in one phase.
strip on RE
28.5 thick, dark amber

+ 75 ml H_2O → 1 phase.
xtrt 2 x 40 ml 30-60 pet ether - back wash c̄ 40 ml H_2O

~~[illegible]~~ H_2O into this - xtrt c̄ [illegible] x CH_2Cl_2
wash 2 x 50 ml H_2O
flash (red oil)
10.8 g thin oil
probably largely sulfolane.
(121A)

there is a red oil interface

pet ether
strip hard

1.47 g pale amber oil - amine smell.

0.04 mm
120 blush.
145 over start
beautiful, FB
160 done

~~[illegible]~~ 1.33 g
6 ml IPA
HCl 22 no 26 yes H^+
xtals at 20 already starting.
add 4 ml ether to aid filtration.
wash c̄ 3/2 IPA/ether
add mi's to 109 D

air dry
1.34 g
check IR - vs impurity

Odds & Ends.

5-MeO-DMT. free base - recryst. warm heptane
→ white (almost) xtals need ms →

0.025 g in .125 ml IPA 1 drop HCl - ether to turbid (20 drops)
no xtals could be gotten

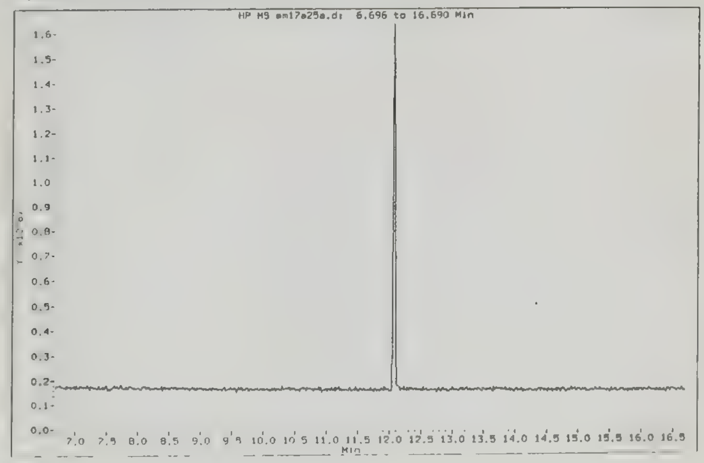
---

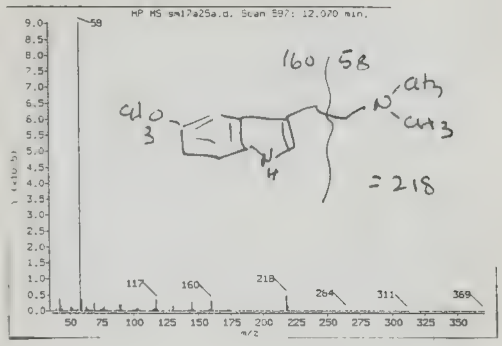
maybe second run of 104?!? E. flask on lab bench ~ month or two, unlabelled. - lots of solids - red - and 20 ml liquid, fluid, strong smell of amine strip → 2.3 g reddish oil.
scrape out solids → 18.1 g
grind under H_2O, CH_2Cl_2 - sep CH_2Cl_2
3.47 g
second CH_2Cl_2 poor
wash c̄ dil NaOH
flash CH_2Cl_2 → 3.47 g
fluid
+ gums. - wash c̄ CH_2Cl_2 (not sol)
transfer to 14/20 RB -
flash - KR to see what will happen.

50-70 lots of white liquid over.
0.04 mm. stop at 90° change flasks.
0.60 g
white.

on - 135° no
by 170° some orange stuff over -
put in dr.
junk!
OUT

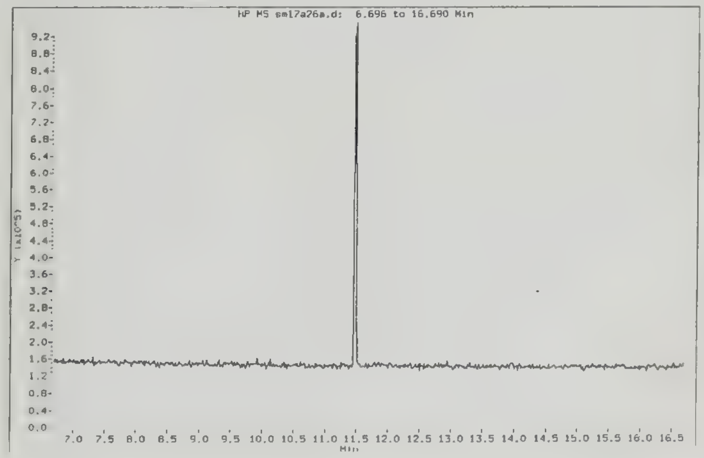
Data File: /chem/med1.i/sm17.b/sm17a25a.d
Injection Date: 07-APR-97 13:25

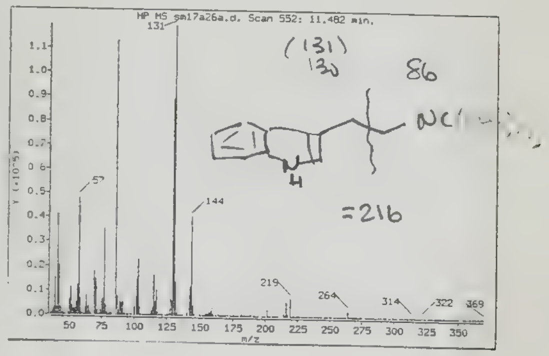




5-MeO-DMT

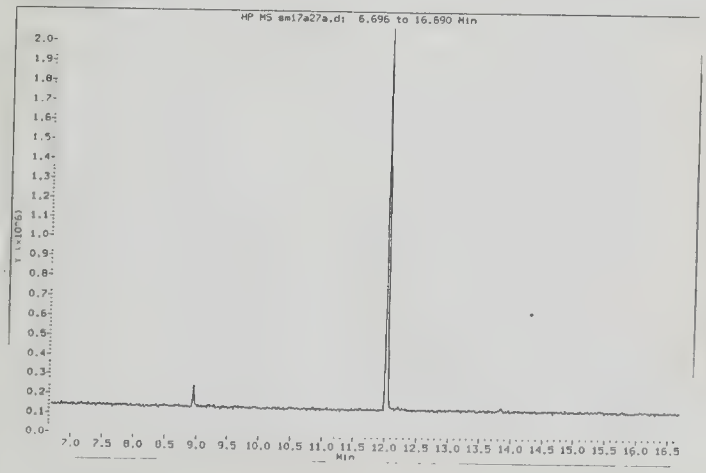
Data File: /chem/med1.i/sm17.b/sm17a26a.d
Injection Date: 07-APR-97 13:48

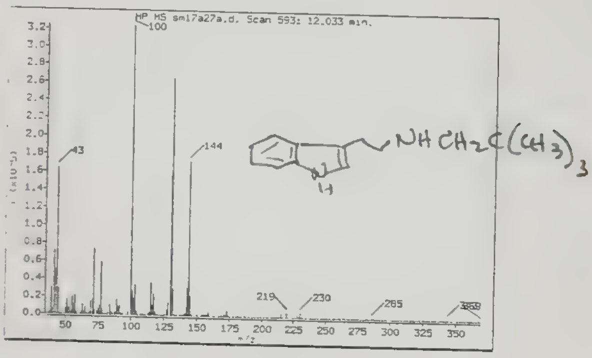




SN-17 A26-A   80mg base VII-17   NTBT

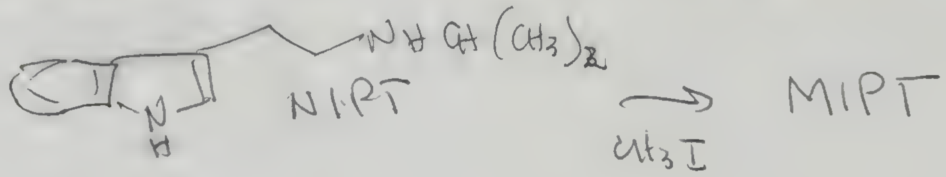
Data File: /chem/med1.i/sm17.b/sm17a27a.d
Injection Date: 07-APR-97 14:11





neopentyl

SN-17 A27A   VII-31   NNPT

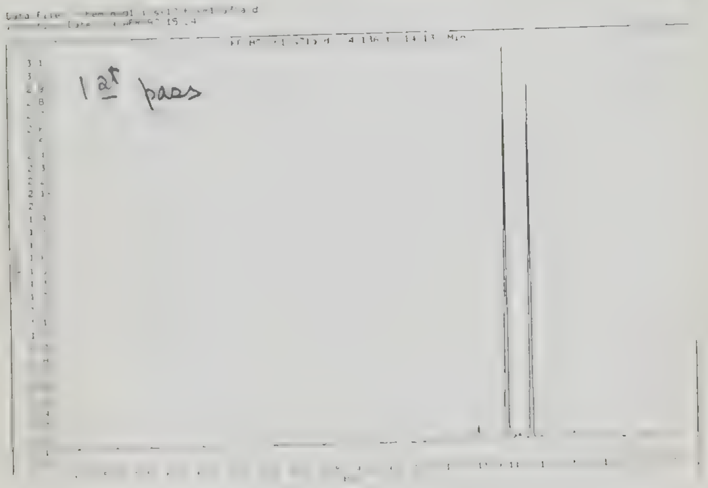


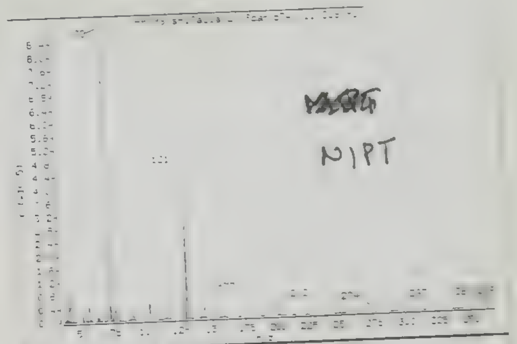
0.47 g (2mM) NIPT·HCl into 50 mL H2O, 5% NaOH – xtrt c̄ CH_2Cl_2 (3 × 40 mL) flash → 0.43 g oil · xtals?!

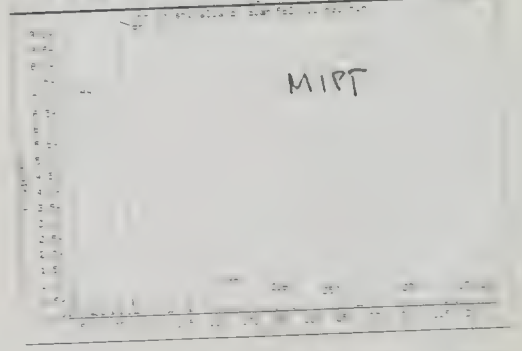
into 25 mL IPA.
+ 0.35 g CH_3I (25% xs) 0.28 = – Δ s13 3 hrs → dry!

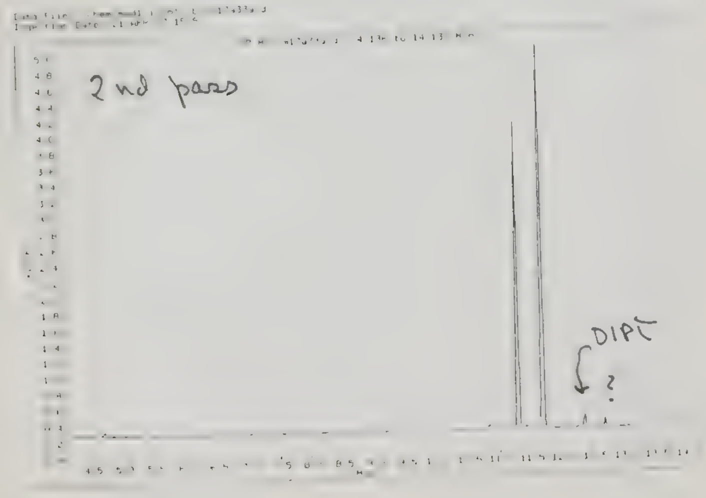
TLC some NIPT – lotsa MIPT – into 10 mL IPA – + 0.14 g CH_3I (25% xs → 75% xs) – Δ 55° – let stand

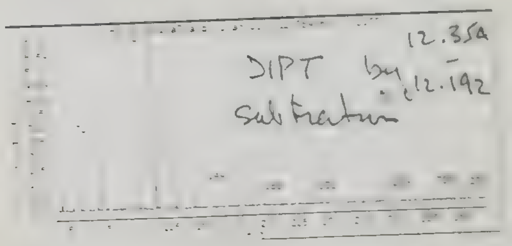
... oil, 25 mL IPA 0.35 g CH_3I







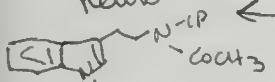




let stand a few days - cloudy - then xtals come out. fine plates - filter → xtals. great ?

strip - partition between 5 N NaOH & CH_2Cl_2 - sep. wash aq. c̄ CH_2Cl_2
pool - flash → 0.23 g oil + 0.5 g Ac_2O.

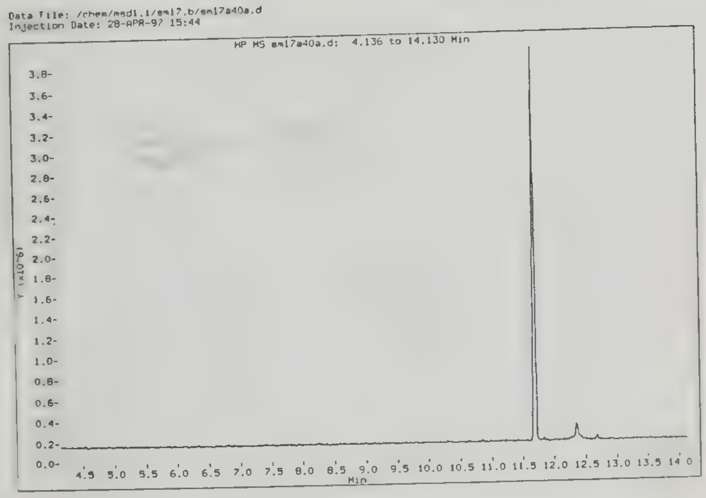
ΔSB ~ 1 hr. ▽ → lots of 5% NaOH -
xtract c̄ 3 × 40 ml CH_2Cl_2
neutral! ← xtract CH_2Cl_2 c̄ 3 × 40 ml 1N H_2SO_4 - pool - OH^- c̄ 5% NaOH
xtract c̄ 3 × 40 ml CH_2Cl_2

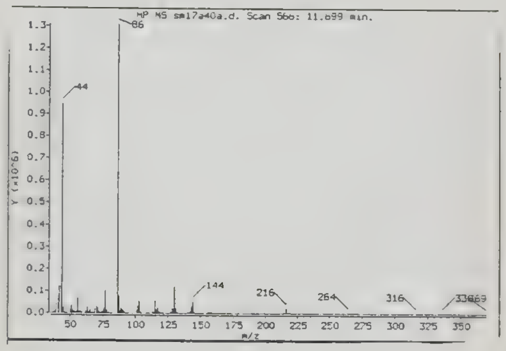


30 mg

→ 0.12 g colorless oil.

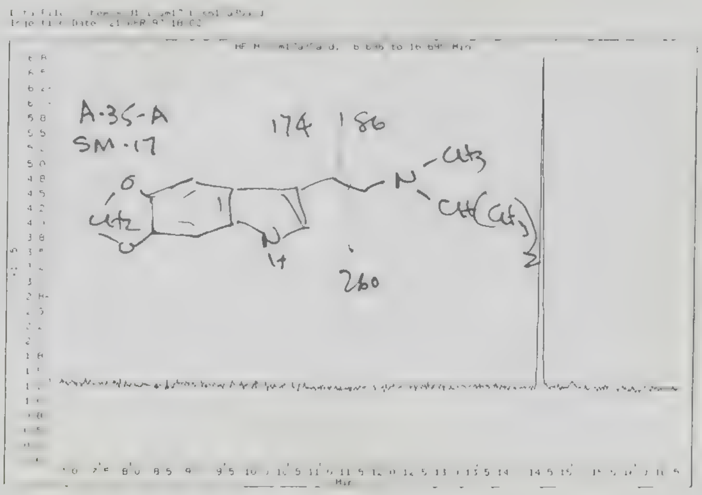
Kf. 0.1 Micron.
135° in. 140-150 - to 170 - nomore. clean pot.
→ 60 mg white oil looks fine. xtals!

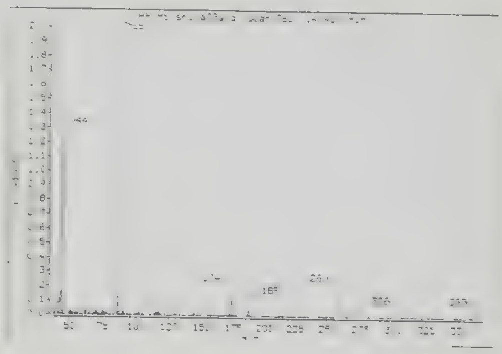


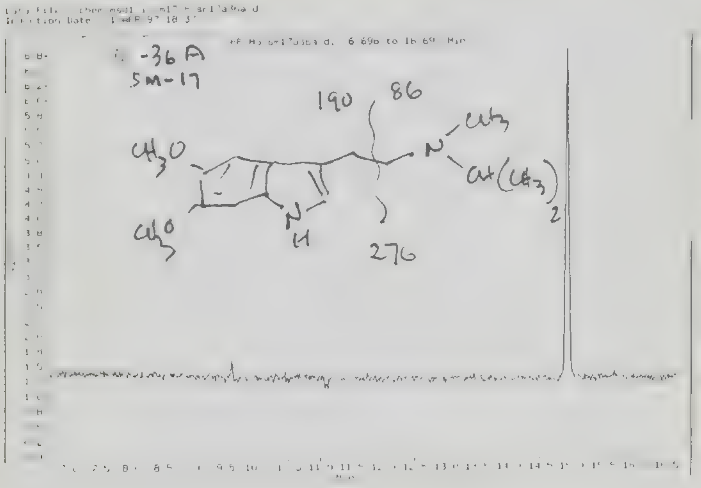


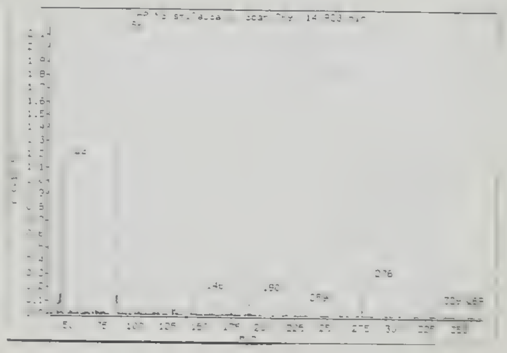
(126)

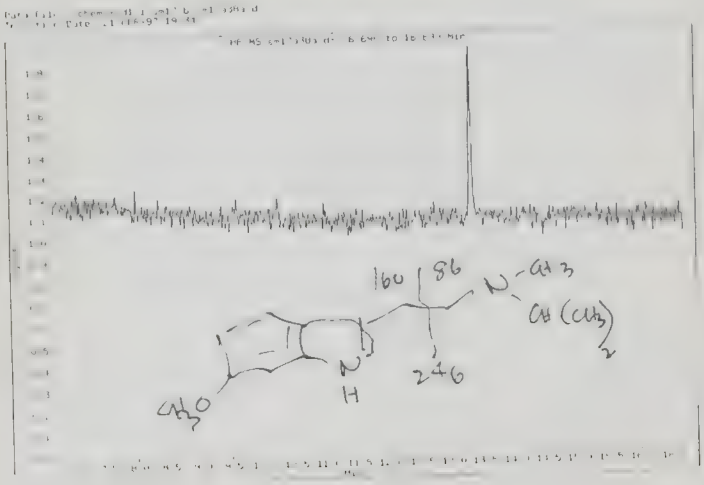
Spectra from here & there

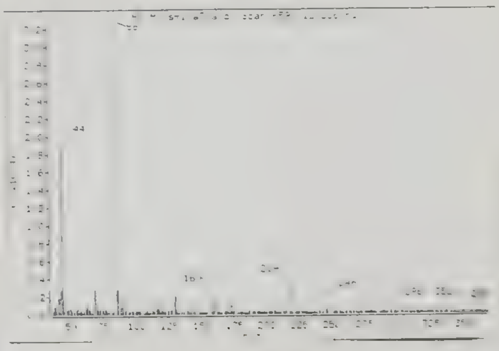






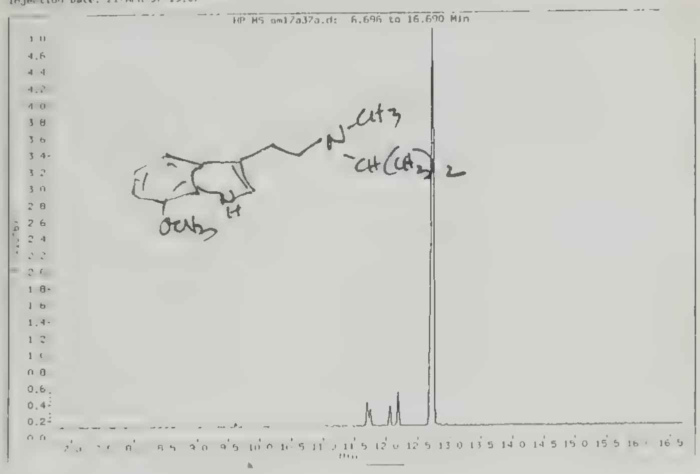






7-MeO-MIPT spectra

Data File: /chem/msd1.i/sm17.b/sm17a37a.d
Injection Date: 21-APR-97 19:07



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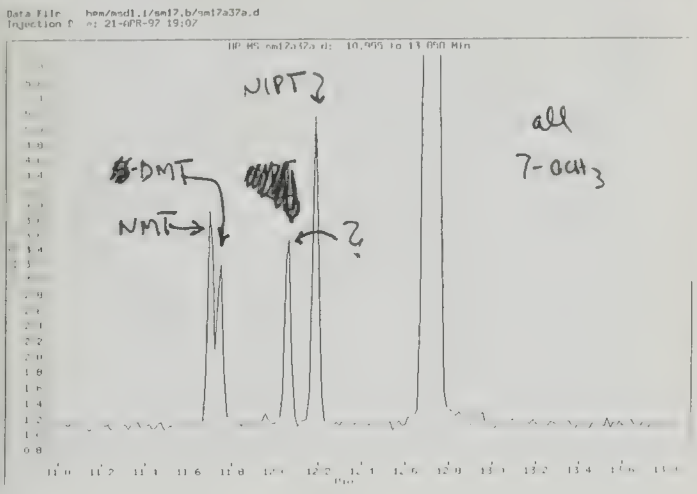
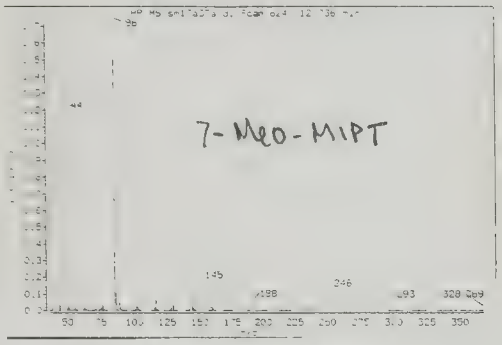
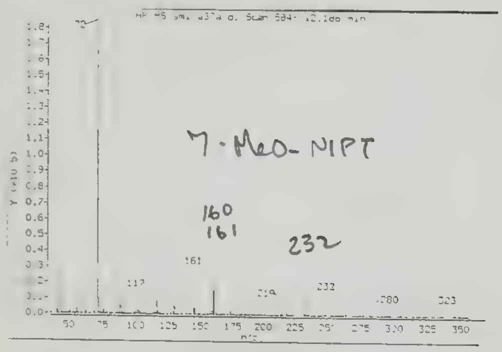
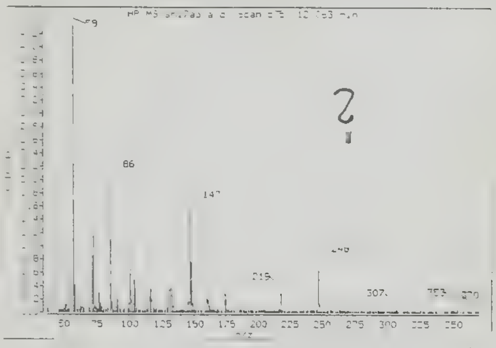
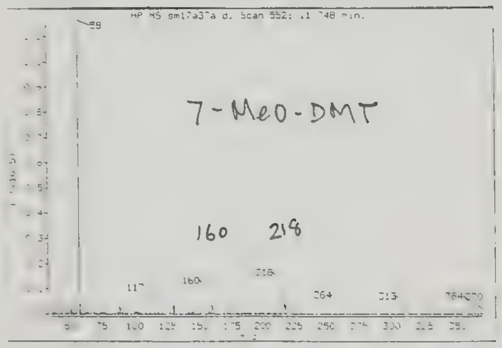
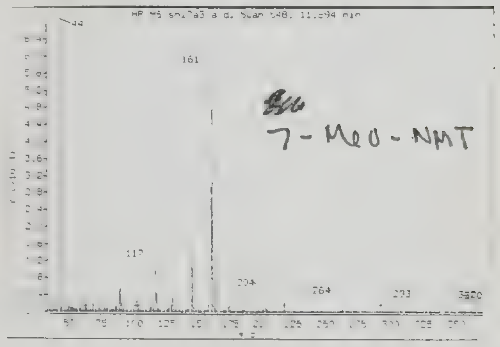








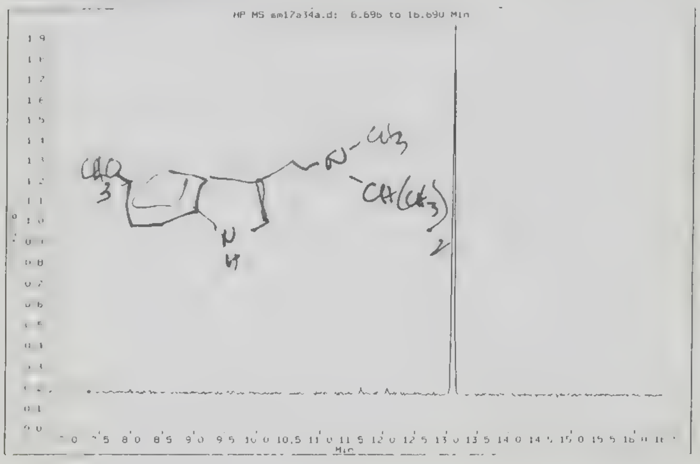


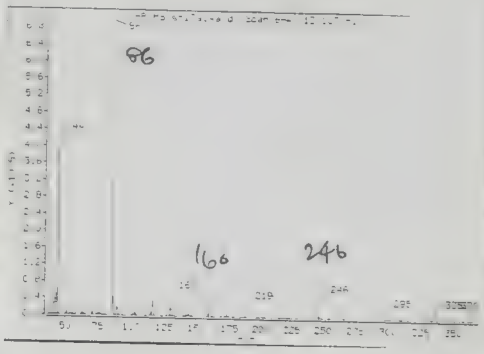


(128)

more from here and there.

Data File: /chem/madl.i/am17.b/am17a34a.d
Injection Date: 21-APR-97 16:2?





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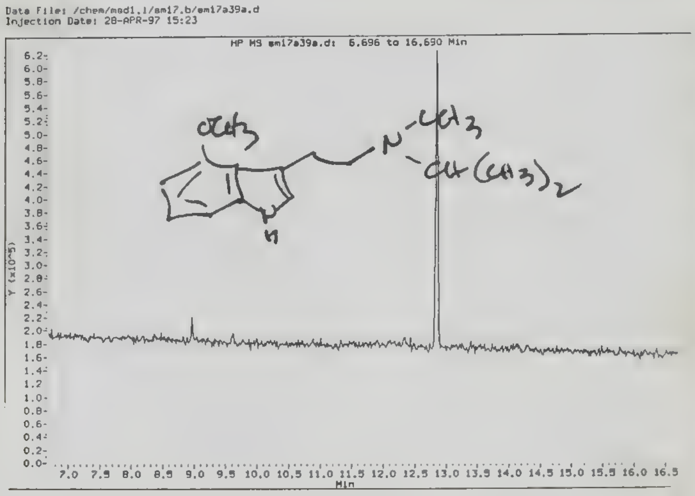
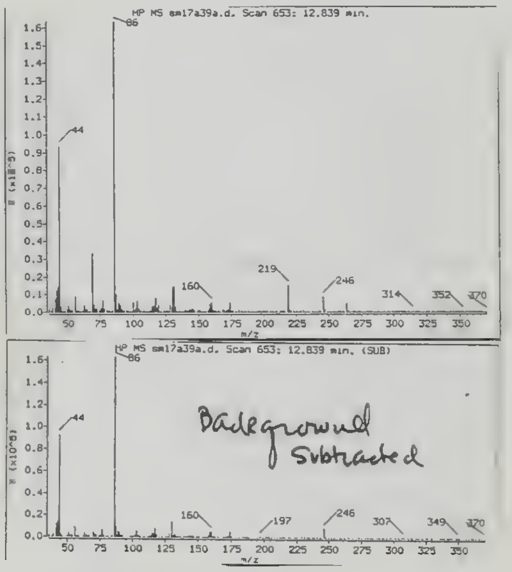
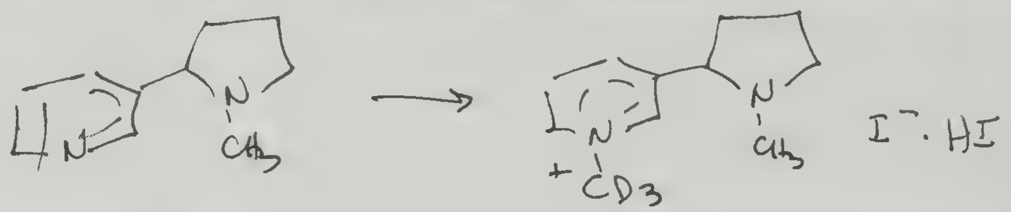




(130)



Weights.
nicotine 162
·HI 290
.2HI 418
Cotinine 176
CD_3I 145

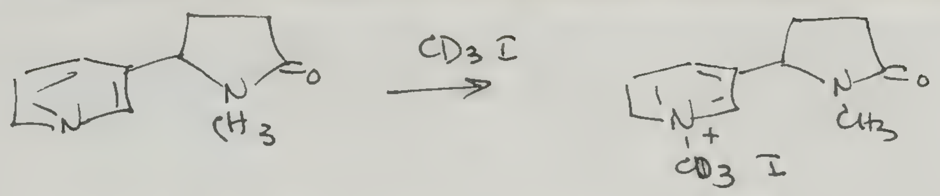
Follow CT
Dec 19, 1979
p70

2.5 g nicotine – 30 ml anh. EtOH
(theo ~ 8 g 50% HI)
at 6.7 g pretty red – add the rest anyway
+20 ml ether, EtOH, ether back & forth.
no xtals
onto RE – hard evaporate → yellow xtals.
6.48 g yellow solids (130 A)

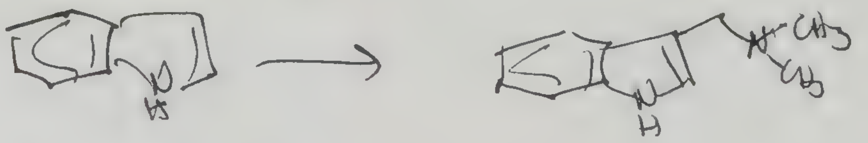
3.58 g Nic · 2HI
1.38 g Nicotine in
30 ml EtOH
1.21 g CD_3I
} onto reflux – 2 hrs ; ∇ → xtals

filter → 3.30 g yellow solids
(stand a week, minus sample to S.F.) → 3.18 g

quat
Nic CD_3^+ I^- · HI (130 B)



0.85 g cotinine - into
1.5 ML MeOH



To 20 g aq. $NHMe_2 \cdot HCl$ (sat soln - delegues stuff) add
20 ml 50% base → 40 ml ~25% $NH(Me)_2$ in H_2O (+ salt)

▽ in ice bath. add
30 ml HOAc add
17.2 g cold 37% HCHO
add all of this, to
23.4 g indole xtals - stir (slightly exothermic -
stir ON. - in AM dump into
40 g KOH in 300 ml H_2O,
↳ yellow gum - GCMS of gum
mostly indole + gramine
a bit skatole, a bit 1-mannich -
a bit late bis mannich (1 & 3).

stand a day
decant aq → fine white xtals ← save seed ← not used yet
heavy yellow solidifying oil (save seed) - into ~100 ml
CH_2Cl_2 - separate, xtract aq. c̄ CH_2Cl_2
pool - xtract 1×200
1×100 ml 1N H_2SO_4
wash c̄ CH_2Cl_2 (still cloudy) CH_2Cl_2 yellow
aq. colorless

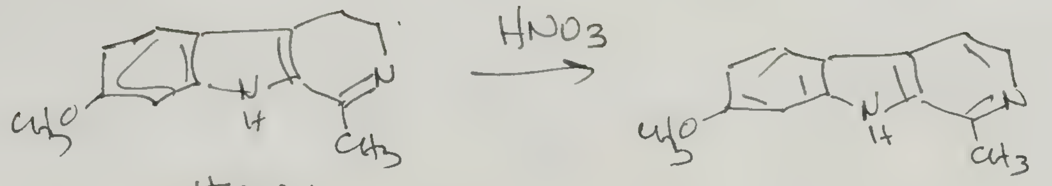
make basic c̄ 25% base → pH ↑10, solids!
cloudy! -

xtract 3 × 75 ml CH_2Cl_2 pool flash
↳ 7.7 g almost white solids

spilled some getting H_2SO_4 away from pooled CH_2Cl_2's
much white solids behind at "not used yet"
yet a lot of CH_2Cl_2 insoluble
dil H_2SO_4 insol
acetone insol
MeOH soluble stuff discarded from sep funnel

yield ~11 g.
recryst from acetone - beautiful white mp 131-132

(Tryptamine, ex CH_3CN (fine) 112-114°) (old 5-MeODMT 58-61°)



, HCl . 2H₂O = 286.5 . HCl . H₂O = 266.5

Base 212

[0.5 g harmaline . HCl in
8 ml abs EtOH
8 ml conc - HCl] to this, add

[0.25 ml d 1.42 conc. HNO₃ in
7 ml abs EtOH]

Δ S.B. – almost hot – bubble bubble bubble ! –
30 seconds – off – ∇ c̄ cold water → xtals stand 2 hrs

filter – wash c̄ bit of EtOH (acetone would have been better)

air-dry ON → 0.31 g pale yellow xtals. (67% Y)
IR ≡ absolutely c̄ aldrich reference spectrum.

Save a small as seed (133A) mp 267°

rest – to free base for GC cleanliness
verify IR,

dissolve in 3.4 ml RT H₂O, 3.1 would have been OK. add ~ 6-8 drops conc NH₄OH →
globs of almost white solids
grind, stir, breakup, filter
→ let air dry, no 100° dry

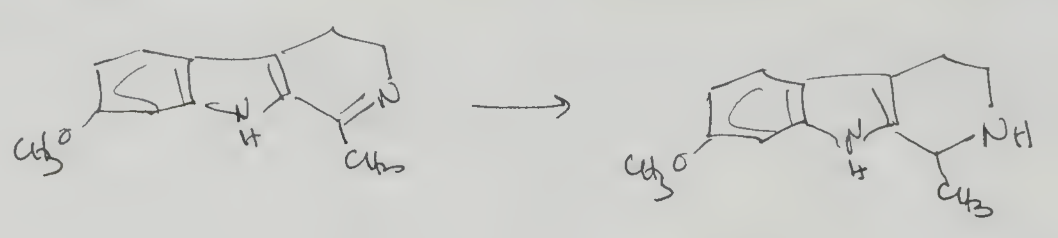
small sample – without purification
for IR
for GCMS

(133B) 0.22 g off-white solids

mp 253° dec ?

134

|| to page 44



1g $H_2 \cdot HCl$ mw 250 = 4 mM — into 25 ml H_2O almost clear solution pale orange.

add (under Argon)

100 mg PtO_2 — stir

add

400 mg $NaBH_4$ in 4.0 soln (3.6 H_2O) a few drops at a time

added 1N HCl as needed to keep Rx acidic

(a lot more than 4 ml which was what I thought would be needed.

20 minutes

Rx looks almost colorless (PtO_2 in way)

filter through paper → pale yellow filtrate - wash c H_2O - make basic c NaOH → white cloudy.

xhT c 3×50 ml ether

1st white solids xtalise

2,3 not so.

flask on R.E. → 0.88 g white! solids.

scrape out → 0.60 g.

— flask residues c ~10 ml MeOH

Δ SB, ∇ - xtals filter off. → spectacular long xtals

134A. 0.05 g reference, GCMS, mp, IR

mp ← 187-9 (theo 200-1)

.88

12 g IPA 8-12 drops HCl

Δ → sol.

Start RT 1 day

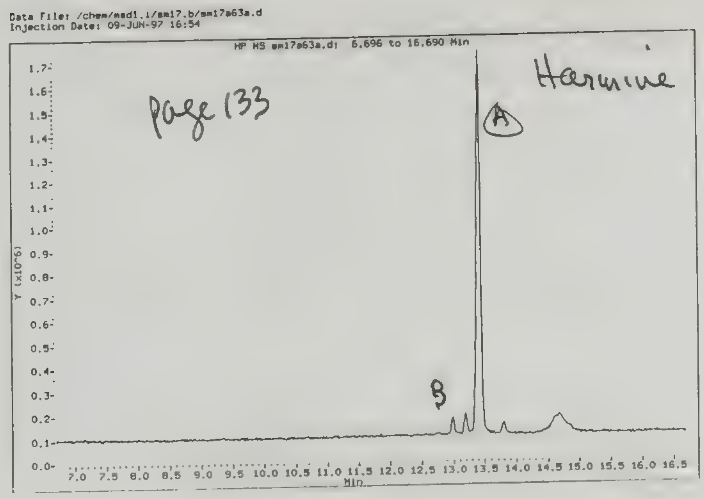
filter, wash c IPA

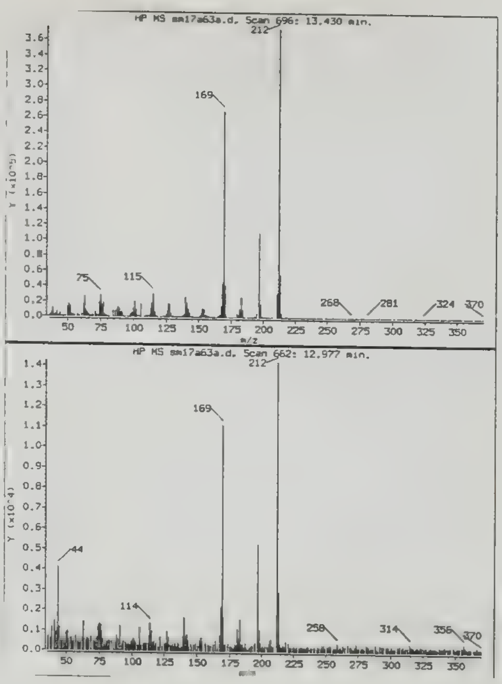
→ 0.53 g greenish xtals when 100° dried

75% Y (134B)

mp 232-234°

Data File: /chem/msd1.i/sm17.b/sm17a63a.d
Injection Date: 09-JUN-97 16:54





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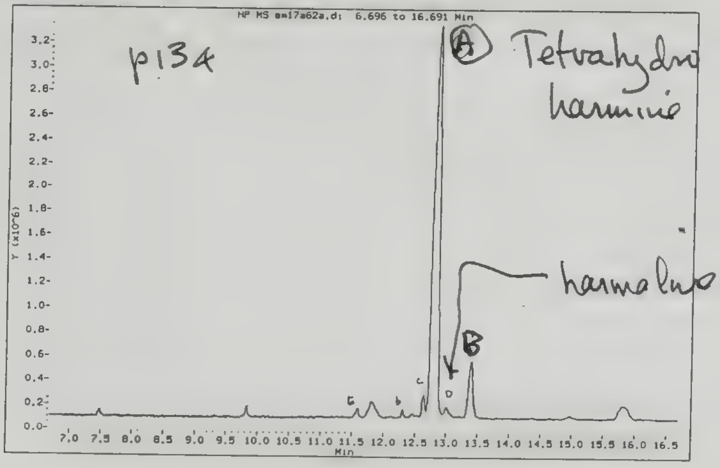
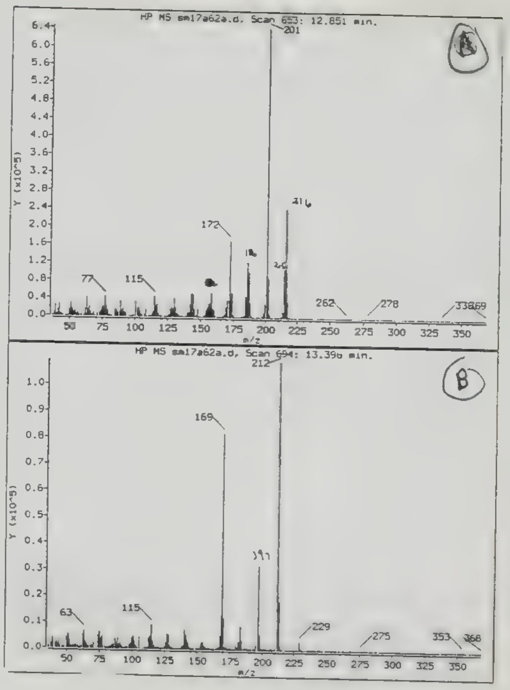
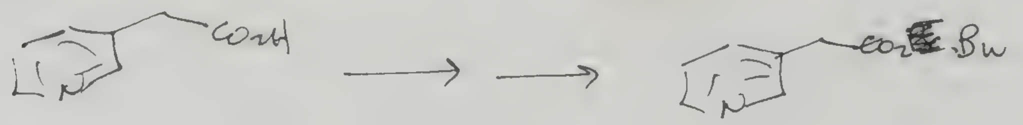






#1 200 mg Pyridine acetic acid, into
6 ml MTBE. not sol, Δ part sol, ∇ part sol. add
0.4 ml oxalylchloride - stir - some Rx? - Δ SB - no
different. Add 0.8 ml BuOH. - Δ briefly SB.
add 25 ml sat $NaHCO_3$ + drops of sat Na_2CO_3 until
pH → green on paper (40 drops).
Xtrt 1 × 20 ml CH_2Cl_2 flash → 0.46 g white oil.
pump more → still 0.46 g
ester smell - no BuOH.

#2 as above - no solvent. - change solid character. add 0.8 BuOH.
knocked over, lose most.

Isolation of things from red-blossomed T. grandiflorus.

66 g of shredded plant (maybe one dose, 1½" dia, 6" length)
66 ml 25% NaOH – homogeneous in 2 days – stir 1 week
xtrt 2 × 66 ml $CHCl_3$

→ $CHCl_3$ greenish
xtrt 2 × 66 ml 10% HCl

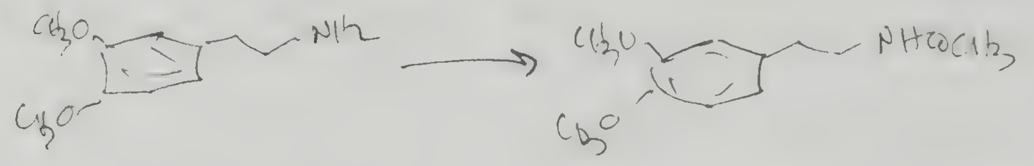
→ $CHCl_3$
flash
↓
0.38 g. oily film
(137A)
0.29 on standing.
OUT

→ H^+ aqueous
pale green
OH^- c̄ 25% NaOH
when pH base,
green → pale yellow?
cloudy. (even before neutral)
▽ to RT.
extract 2×
~25 ml CH_2Cl_2
flash
↓
(137B) alkaloid fraction.
0 weight
GCMS
See cactus notebooks
page 24

→ aqueous yellowish
neutralize c̄ HCl (conc)
juggle c̄ 5% NaOH until neut.
+ 60 ml sat $NaHCO_3$
(pale green pH falls
pale yellow soln.
Zwitterion fraction
0.03 g
filmy solids
(137C)
→ See MS p152
aqueous neut c̄ HCl
add HCl to ~10:1
aq. HCl
~1 N.
Stand a few days.
Δ SB 2 hrs
RT ON

137C – save a bit for GCMS
rest (47 mg) c̄ Ac_2O & pyridine

(138)



1.8 g amine (sol'd i cool'mat, out of the bottle i a pipette) into

3 g pyridine - add

1.2 g Ac_2O (1.02 eq)

quite warm, wait until it cools, into ~50 ml H_2O
acidify i conc HCl - xtrt i CH_2Cl_2 (2 x 50 ml)
pool ~~extract~~ wash i sat $NaHCO_3$ - mess - clear - wash i H_2O.
shake,

flash CH_2Cl_2 (acid washed, base washed H_2O washed)

→ 1.72 g pale yellow oil.
GCMS sample
(138 A)

add 1.7 g polyphosphoric acid.

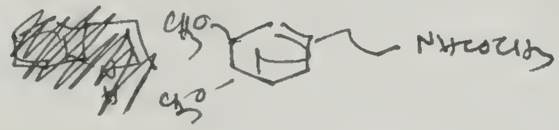
Δ SB - 1/2 hr.
+ 3 ml H_2O - 1/2 hr more.
xtrt i 2 x 50 ml CH_2Cl_2

I have forgotten what I did. CH_2Cl_2 into base? (?) basic, into CH_2Cl_2?

flash CH_2Cl_2 → 1.41 g brown oil (138 B)
$NaBH_4$.

from (138)

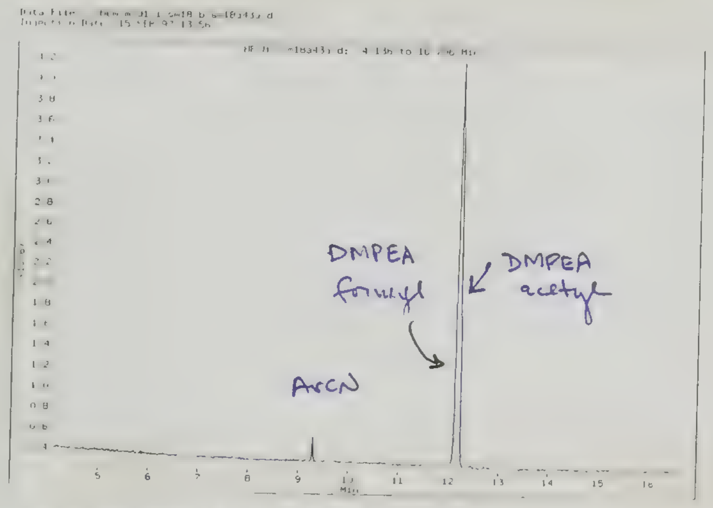
Final product → 1.14g amber oil.
distill. 0.2 mm/Hg no 60°
130°
150 ~~[…]~~° no / 0.1 mm
160 → 170° ! → 0.90 oil white xtals.

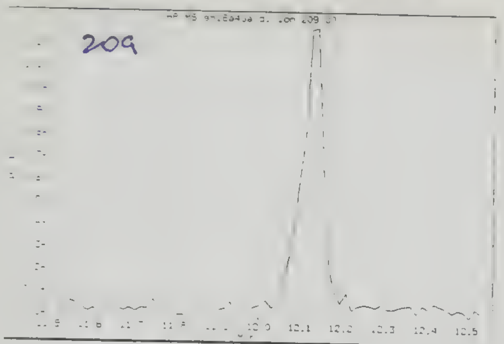
This is the amide 

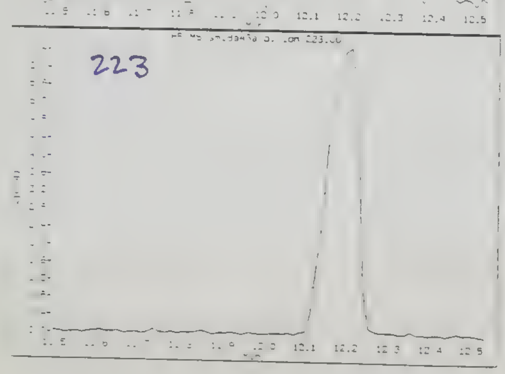
remove 0.64 p 140
remains 0.74 here

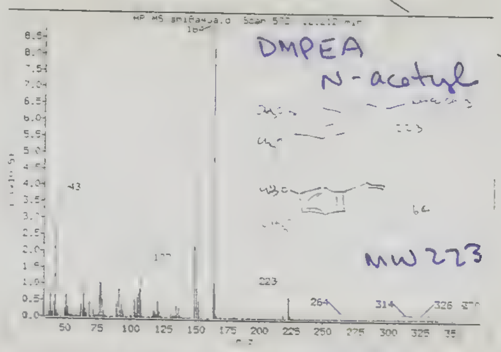
(139)

See page (141)
hexane insol.
cyclohex. insol.
meoh too sol.

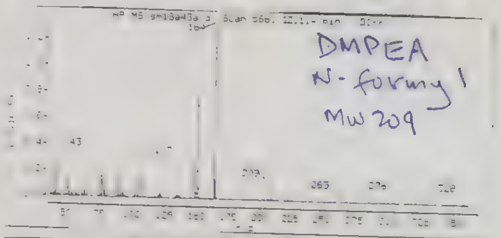




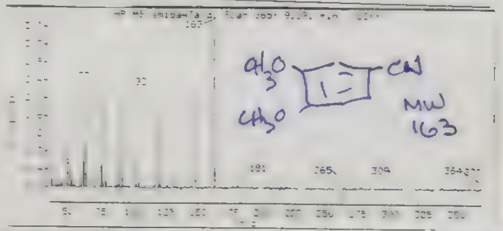




12.212 min

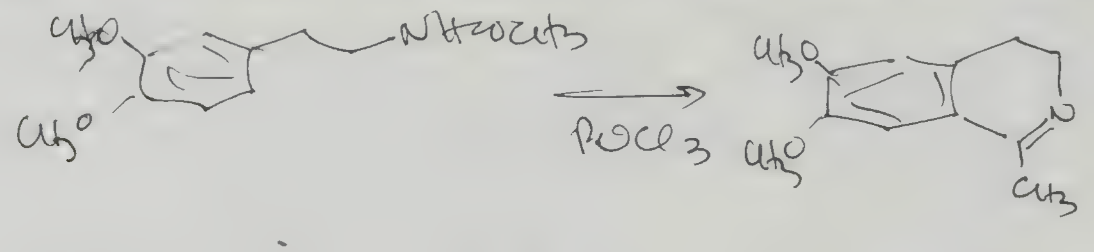


12.114 min
difference



9.291 min

(140)



0.64 g white distilled solid (p 139). add
1.5 g $POCl_3$ (may be old - screw-cap cracked)
Δ SB 1 hr → deep red-brown
add 20 ml H_2O stand ON
add more water. (strongly H^+)
extract CH_2Cl_2
2 × 25 ml

make basic
c 5% N NaOH
xtrct 2 × 25 ml
CH_2Cl_2

CH_2Cl_2
most of the brown color

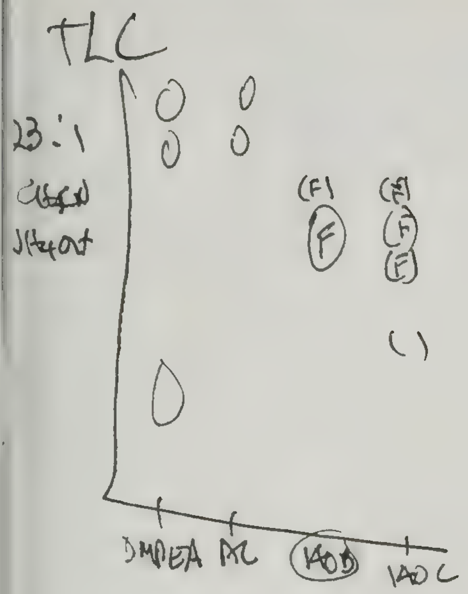
0.11 g black oil
smudges
(140A) OUT

repeat page 144
flash
0.49 g
pale off-white solids!
wow!
(140B)
Save 100 mg
the rest, reduce.

into dilute ← 0.39 g
HCl
+ xs xs $NaBH_4$
strong yellow → pale yellow
OH^- xtrt - flash -

→ 0.35 g @ 130-140°/0.5 microns
140 C.

TLC



Repeat - weighed & watched. DMPEA → acetamide p 138

3.6 g amine (+ carbonate) ~20 mM
6 g pyridine
2.4 g Ac₂O → onto SB ~10 minutes. ∇ +100 ml H₂O -
make strongly basic c̄ 25% NaOH - xtrt 3× 25 ml CH₂Cl₂
color into CH₂Cl₂ (amber) - wash 2× HCl (both pH 1 ...)
flash → 3.44 g amber oil
→ 2.46 g white oil 170°-190° / 0.2 mm/Hg xtals
all to page 144.

See GCMS
page 139

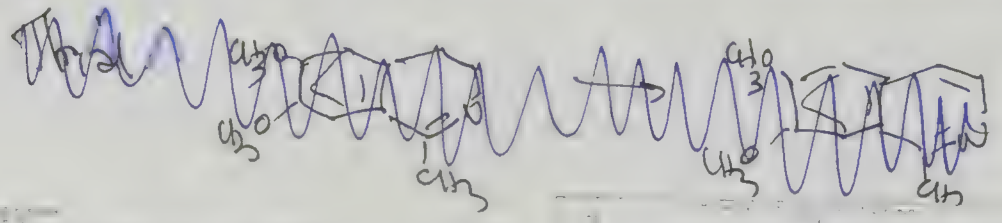
0.15 mm/Hg.

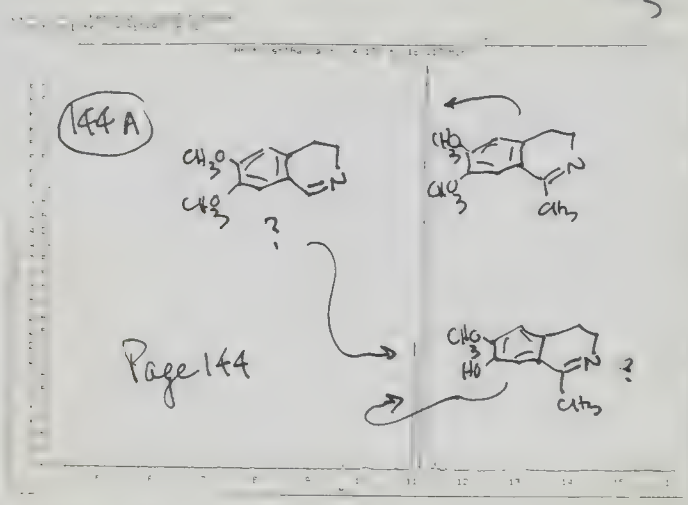
150° 0.2 no.
170° white oil
180° considerable pot
190° still considerable pot off

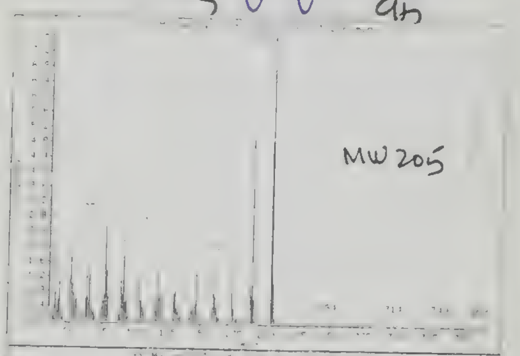
an aside - characterize this
amide 0.13 g from p 139

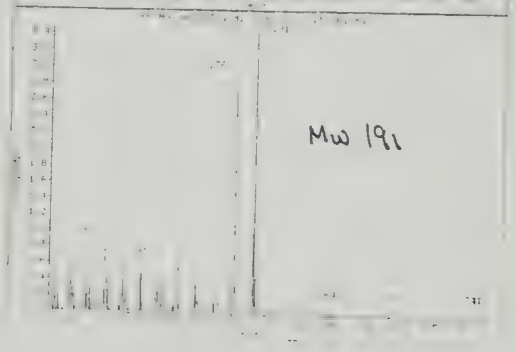
~~[struck through]~~
dissolve in 0.13 g boiling EtOAc.
let cool → magnificent xtals.
filter (p. plate) - wash
lightly c̄ EtOAc.

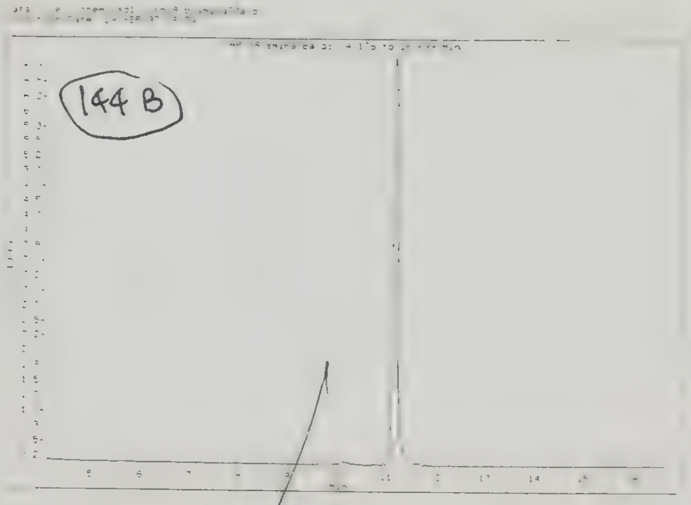
mp 97-98°.
run IR.
run GCMS.





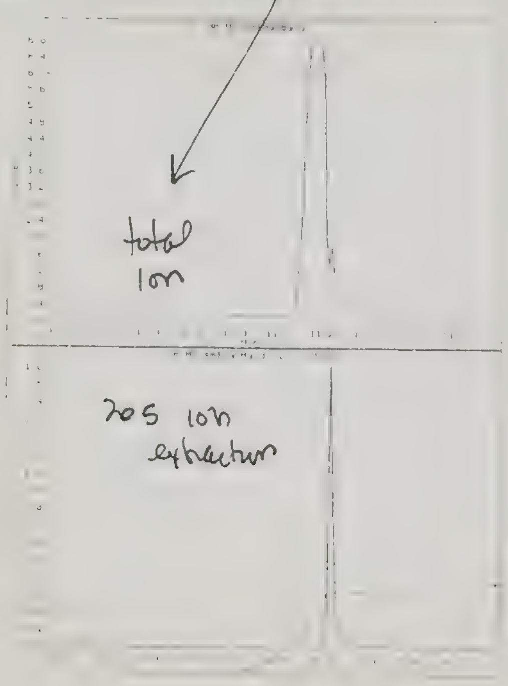


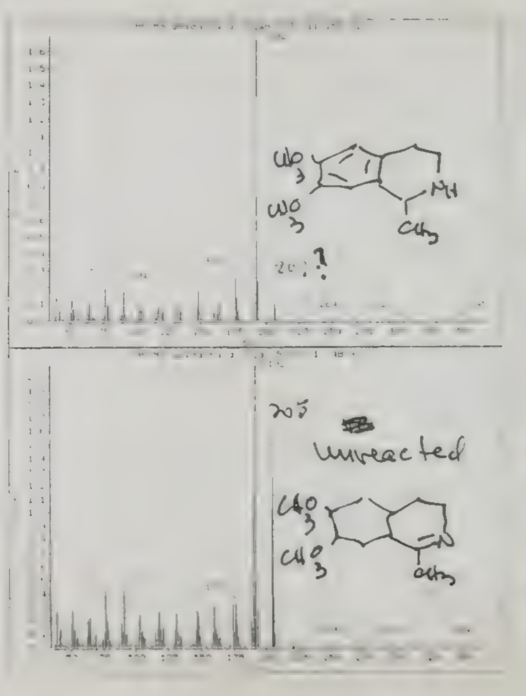




page 144 A

page 144 B





No
see other ②

No!!
See ref
all data

Trial

from page 144

part of 0.84 g white solid, fused xtals.

0.40 g. of distilled "-ane" = ~ < 2 mM.

1.0 ml 38% (40%) CH_2O aq. = ~13 mM

0.5 g $NaBH_4$ = ~ 13 mM.

AcOH = 60 .05 ml =

6 g = 100 mM

.6 g = 10 mM

.12 g = 2 mM = 2 drops-+

into 20 ml H_2O

+ 4 drops HOAc

+ 1 ml 38% H_2CO ~~foaming~~. stirring magnetically.

+ 0.6 g $NaBH_4$ – a dash at a time – foaming.

all in. basic + ~30 drops HOAc → pH 7

stir ~ 30 minutes – add

5% NaOH → pH blue. xtract 2 x 25 ml CH_2Cl_2

flash. 0.49 g white oil.

< 0.1 Hg

0.05 Hg 105-120°. → 0.36 g white oil ~~...~~ 143 #143

+ 78% 1Me 2Me

20% 1Me 2H

traces N,N-dimethyl DMPEA

traces MW 219

turning slowly yellow on standing – no CO_2.

deep brown in 4 months.

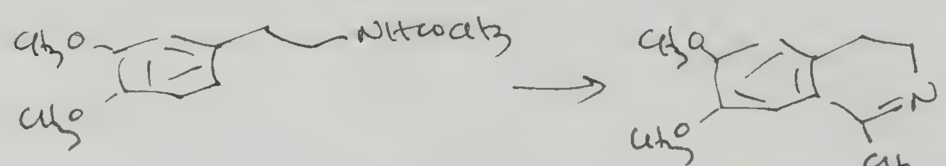
into sint. vial

save 143

See spectra 162

(144) repeat of page 140

See spectra p142



2.46 g amide (ex 141) (all xtaline) add
10 g $POCl_3$ - onto SB. 1 hr. Killed with water ^100 ml too soon (too hot) & lost a pile of it onto the lab bench

wash acidic aq. c̄ CH_2Cl_2, OH c̄ 25% NaOH - xtrt c̄
1.16. 2 x 50 ml CH_2Cl_2 - flash → 1.16 g residue that is a fine tan solid.

save a small (144) for GCMS. (144A)

test 1.08 g r into water pH to ~4 c̄ HOAc - $NaBH_4$ as small boluses. - add HOAc as needed to keep pH acidic ≤ 7.5 - eventually at 0.6 g BH_4 - This should be another aqueous xtrt - accept as such - wash c̄ 2 x 25 ml HCl.

add $NaBH_4$ spoon by spoon - HOAc as needed to keep acidic.

after ~ gram or two of $NaBH_4$ - aqueous sl. acidic.

← xtrt CH_2Cl_2 (ex acetic acid)

make basic
white wisp
ex NaOH
xtrt c̄ CH_2Cl_2

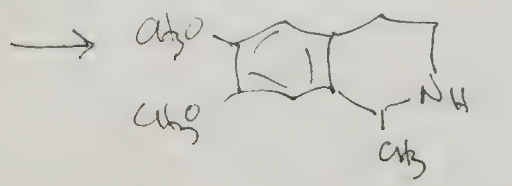
yellow CH_2Cl_2
0.06 g oil -
here is all the amber color

~colorless xtrt. CH_2Cl_2

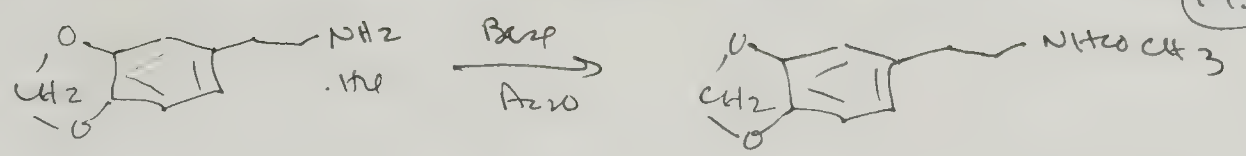
0.9 x oil - almost colorless - distill @ 0.15 mm. 144B

0.15 mm 120° no yes!

130 - 145° → white oil
0.94 in flask xtals
0.84 dug out c̄ breaking receiver. damn.



to page 143



MW 200 = 5 mM

1.0 g MDPEA · HCl ancient reference sample Box 1 A 15!

to 141 — Into 50 ml H2O (brownish soln) + 5% NaOH → blue

xtrt 3 × 25 mL CH2Cl2 flash → 0.82 g tan oil

1.5 g pyridine

0.6 g Ac2O Δ SB ~ 10 min ▽ RT add ~ 40 ml H2O + a couple of mL 25% base. * xtrt c CH2Cl2 2×25 ml

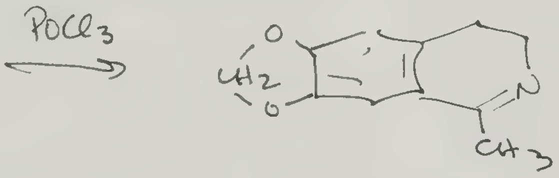
* oil xtalizes save a bit

wash pooled CH2Cl2 c 2×25 ml 1N HCl flash → off-white solids 0.54 g.

GCMS one peak - good stuff see page 150

recrystallize a bit from EtOAc. spectacular

repeat - see 209, 215



0.52 (about) g xtalline amide above c 1.5 g POCl3 onto SB 45 minutes — ▽ to RT, looks like xtals coming out. Is strongly acidic — wash 2 × 25 ml CH2Cl2 — OH⁻ c 25% NaOH - very cloudy - xtrt 2 × 25 ml CH2Cl2 - flash → oil that sets up to fine, almost white xtals

0.70

evap → quite a bit of dark crystals (amide?) 0.17 g under EtOAc gum. c acetone - tan solids. OUT

0.61 g

GCMS Inject on P150 trace of 7,8-isomer trace of aromatic IQ.

See repeat page 216

(146)

0.55 g MDene into 20 mL H_2O + HOAc dropwise until into solution

an equal weight of BH_3^- was added, with periodic drops of HOAc added to maintain ~ neutrality to pH paper. ~ 2 hrs. dilute to 50 mL, OH^- c̄ 25% NaOH

~~Strip~~ 2×25 mL CH_2Cl_2 - strip → .45 g deep amber oil - to K.R. 0.04 mm/Hg 115° → 125° white oil. almost no pot.

0.40 g absolutely white!

~~For the record~~

uncovered old flow. sheet to DMT - 8 g T
14.2 g MeI
13 g [illegible]

all together 2 hr SB
white solids everywhere
into 50 mL H_2O, make strongly basic, xnt CH_2Cl_2, flash,
+ 9 g Ac_2O + 5 g pyridine
ΔSB 20 min + lots H_2O,
25% base - CH_2Cl_2 - xnt
c̄ 1 N HCl - ~~[illegible]~~ to aq. acid
25% NaOH - xnt - flash
→ 1.19 g K.R. 0.05 mm
130° - 145°. - white oil
0.44 g - xtals.
scrap wt. 0.33 g.

isolation from yellow-blossomed
T. grandiflorus.

140 g gooey ground-up cactus - add
140 ml 25% NaOH - stir ~1 month. (2 days - virtually
all into solution - some evap↑ some CO_2↓ add = vol H_2O
extract 50 ml CH_2Cl_2 — have to centrifuge to separate
phases -

CH_2Cl_2 ← → aq.

pale yellow - flash -
weight nil.
into small vol (~1 ml) ϕCH_3
GCMS. on ½ of it. (147A)
other half.
+ a couple of drops pyridine
and a couple of drops Ac_2O
GCMS (147B)

no DMT, gramine obvious.

(148) Do another red-blossomed T. grandiflorus - Red #2
This one for photos, for eventual slides.

one banana-sized cactus 244 g - spines so piercing, the dry-ice glove won't do it! Trim all spines with toe-nail clippers

4.2 g spines + dust + dirt

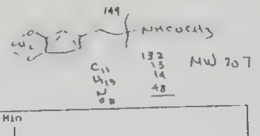
229 g viscous goop. add 400 ml 1.5 N HCl onto steam bath ~3 PM.

Red Do yet another (I think it is red) c̄ mild acid

#3 One relatively large ~8 cm dia, ~25 cm long cactus
472 g, worked up to slimy goop – add = volume (470 mL)
2.5% citric acid solution.

150

from 145A



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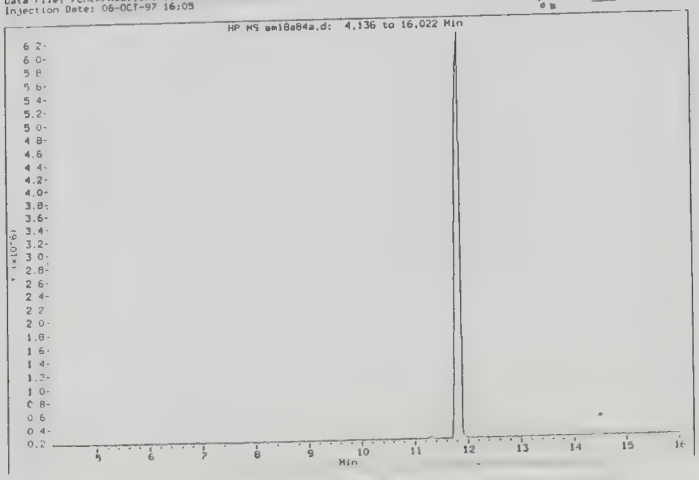
Injection Date: 06-OCT-97 16:05



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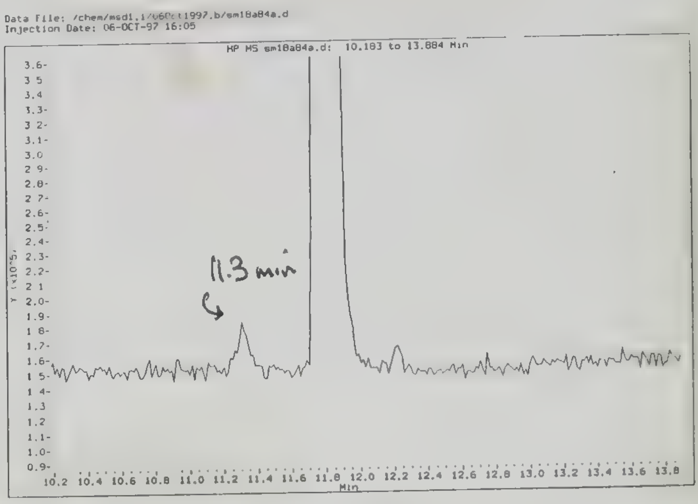
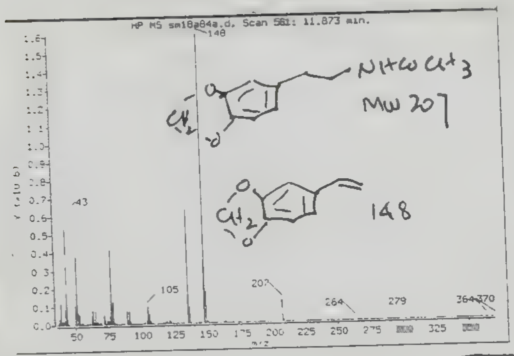
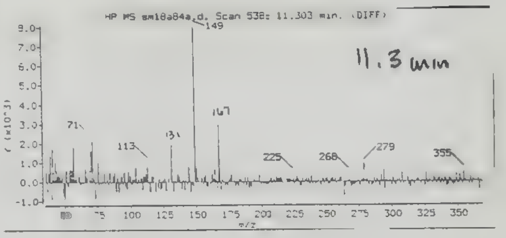


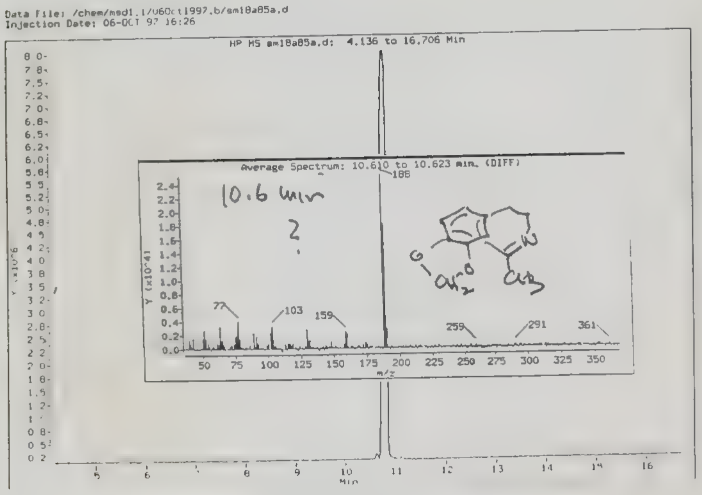




145A ↑

145B ↓

Data File: /chem/msd1.1/06Oct1997.b/sm18a85a.d
Injection Date: 06-OCT-97 16:26



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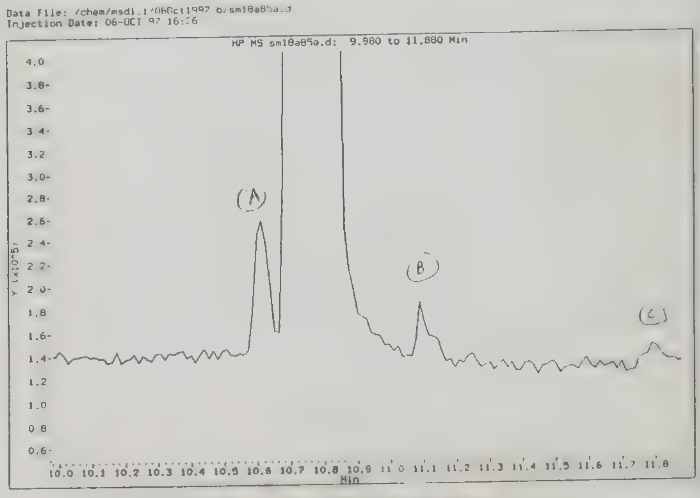
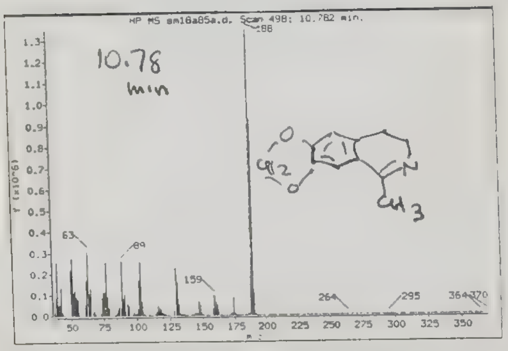
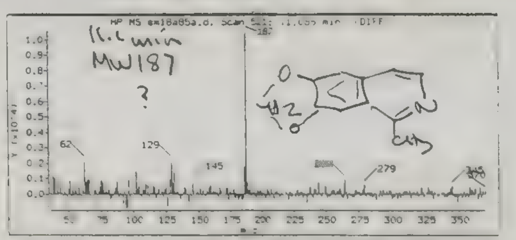
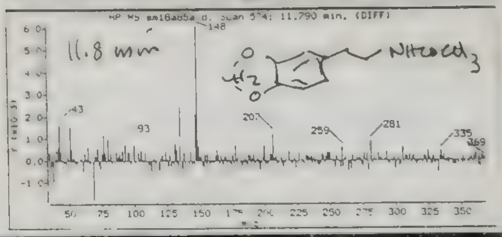


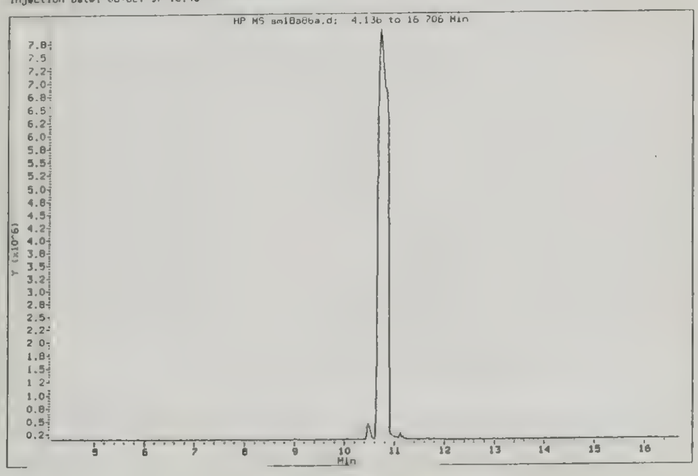




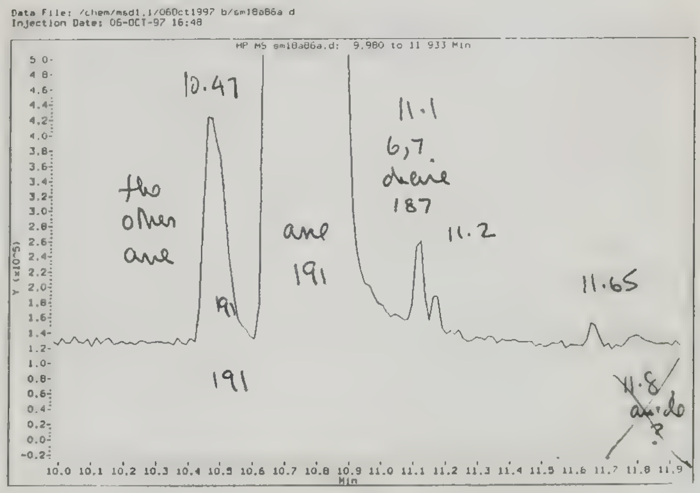


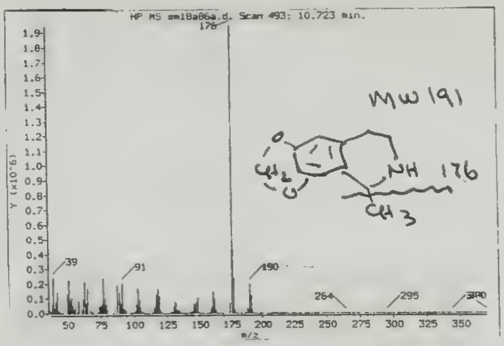
From (146) 6,7 MDO MeH H4 (151)

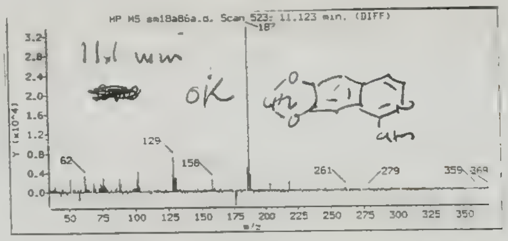
Data File: /chem/msd1.i/06Oct1997.b/sm18a86a.d
Injection Date: 06-OCT-97 16:48

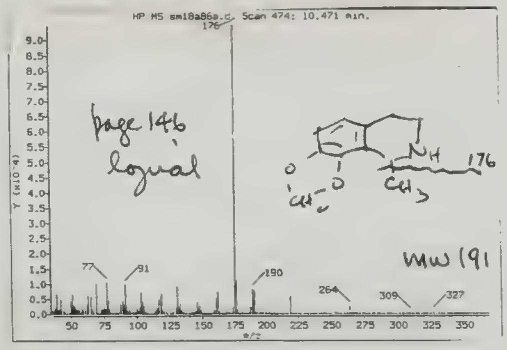


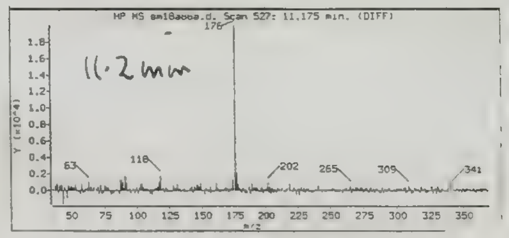
Data File: /chem/msd1.i/06Oct1997.b/sm18a86a.d
Injection Date: 06-OCT-97 16:48

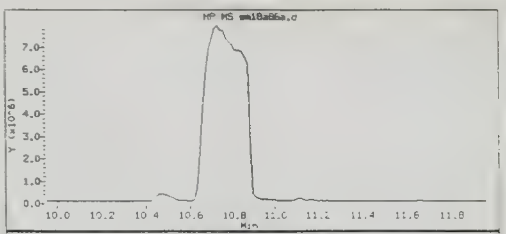


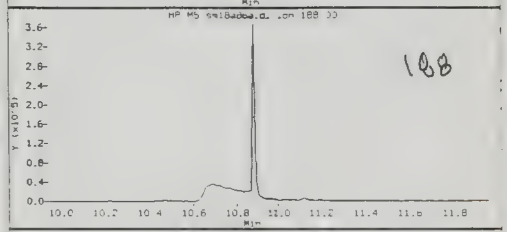


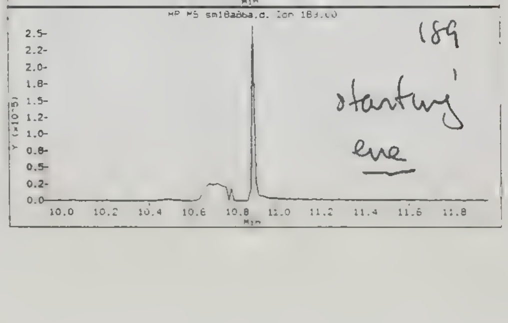


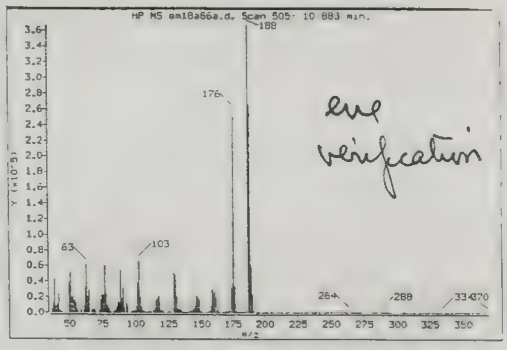




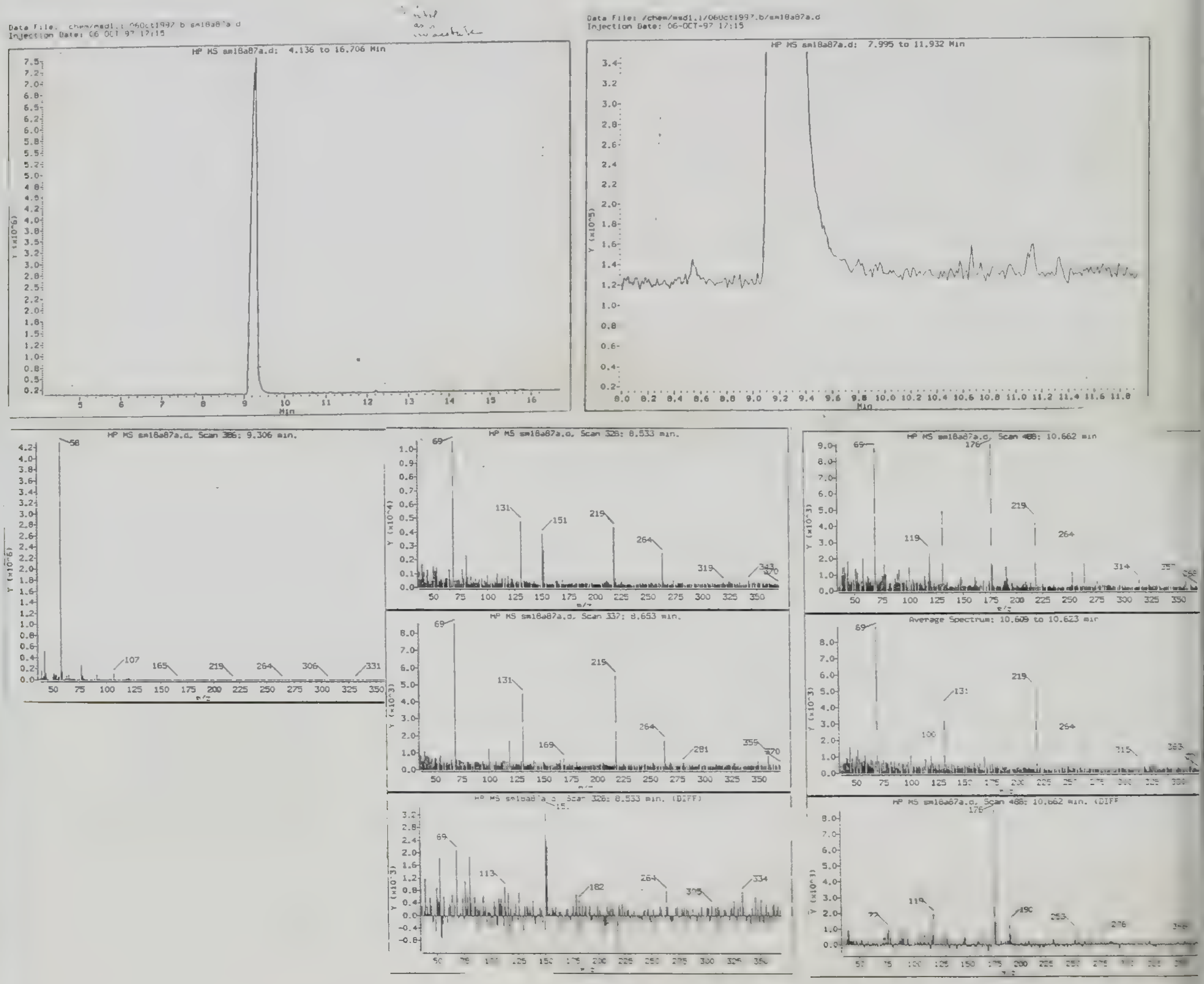






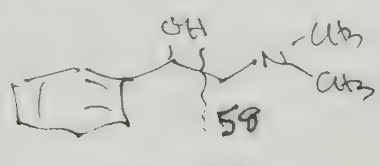


pH 9 fraction from Reed #1 page 137



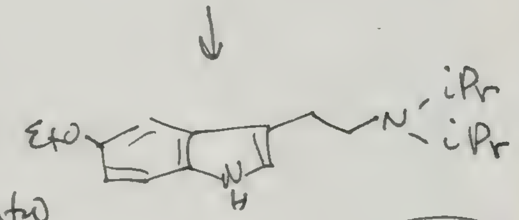
unacetylated
page 137!
solids

?



MW 165

Try!,



(153)

Initially – 5 g 5-HT·HCl to free base, alkylate, O-ethylate –
There you are!

5.16 g serotonin·HCl into ~ 50 ml H2O soluble – make basic c̄ sat NaHCO3 – xtrt c̄ 3 × 50 ml CH2Cl2 → nothing!
pH back to neutral – CH2Cl2 – nothing!

Add a bunch of NH4Cl – extract c̄ CH2Cl2 → something. + a glob of brown gum in sep funnel. – wash c̄ CH2Cl2.

gum + Ac2O (A)

Add 10 ml MeOH – soluble! – flash → 0.4 g puffy film

4 g sulfolane – largely dissolves c̄ Δ.
1.3 g di isopropyl-ethylamine
1.6 g isopropyl iodide. (last of it, reorder)

Δ SB c̄ occasional swirling. 3 hrs.

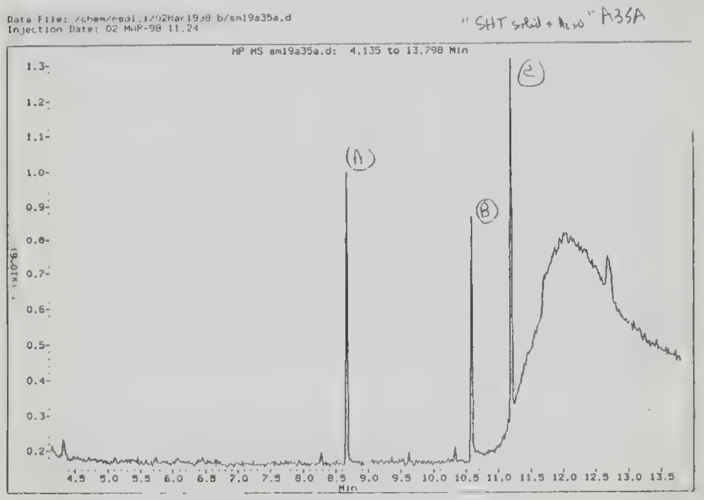
Sample removed – Ac2O (B) ⟶ separate for (GCMS)

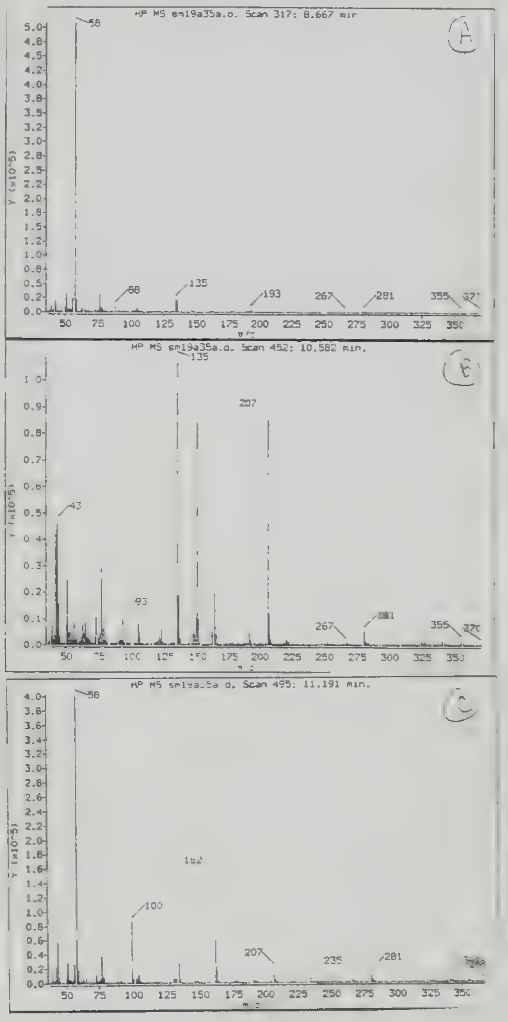
Rest + 3.7 g 25% NaOH
5 g EtBr – stir ON.
a few minutes in SB – . stand ON.

both sample (A) and sample (B) pretty much unrecognizable

See next page

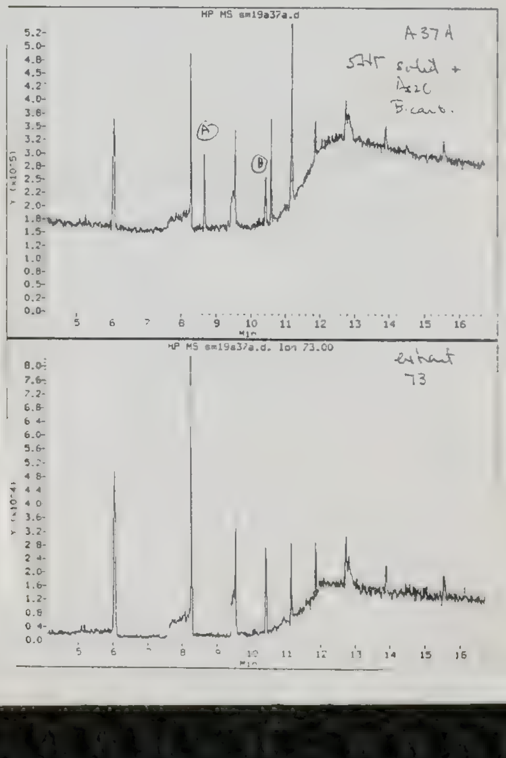
Sample A ("serotonin" & Ac_2O)
page 153

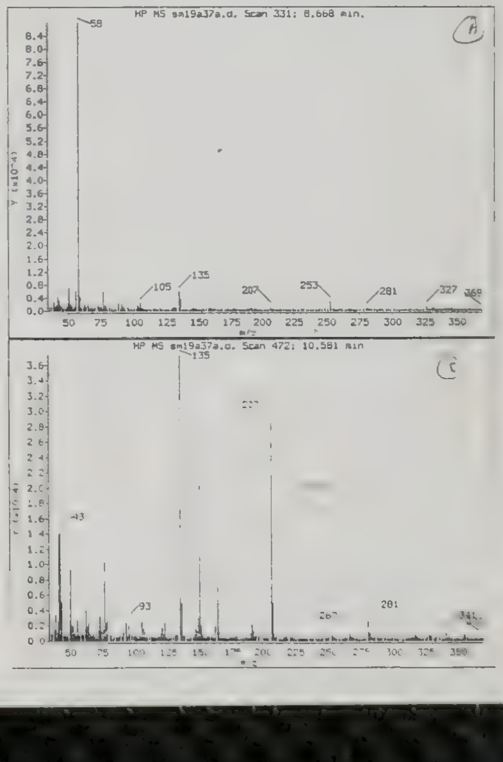




Sample B (after iPrI)
page 153

A37A



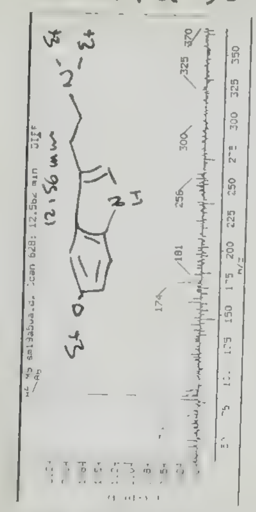


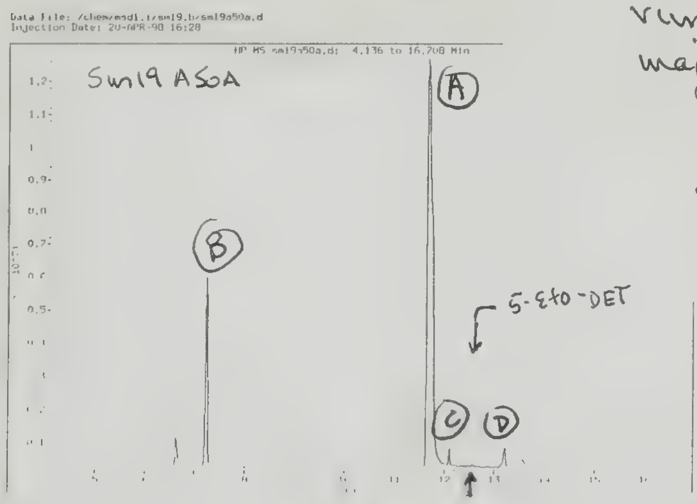
attempt :

10 mM. – under Argon

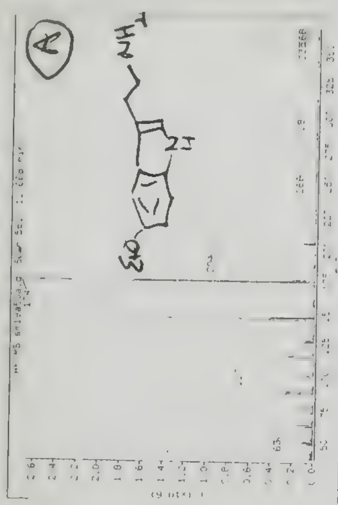
2.12 g serotonin ·HCl in ~ 10 ml H2O, add 25% NaOH
(0.4 g) 1.7 mL neutral won't stir anymore
+ 1.7 mL pretty much goes back into solution
+ 0.5 mL more, for good luck
2.0 g (1.0 mL) (30% xs) EtI.
Stir RT ~ 2 hrs under Argon – not much discoloration
xtrt CH2Cl2 (color stays in aq.) (open to air – rapid darkening).
flash xtrt → almost nothing
run in 90/10 anyway
major product – 5-EtO-T !

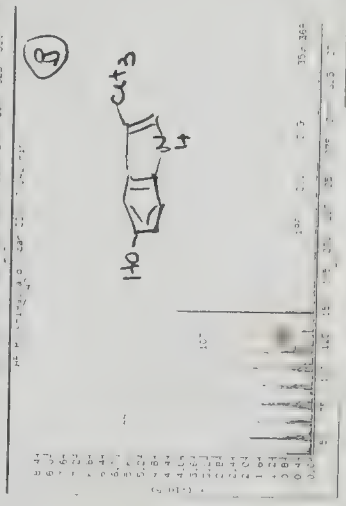
Sm19a50a

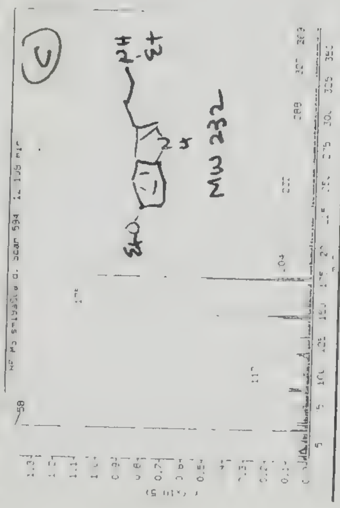


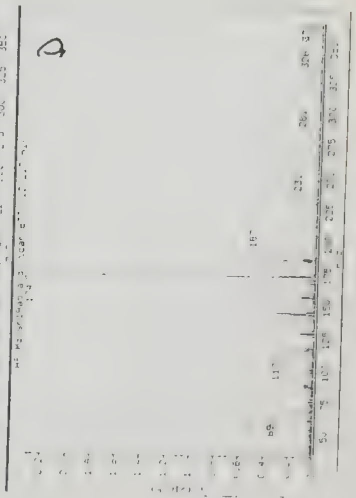


5-EtO-T 11.67 min
5-EtO-NET 12.11 min
5-EtO-DET found by single ion 86
12.56 min

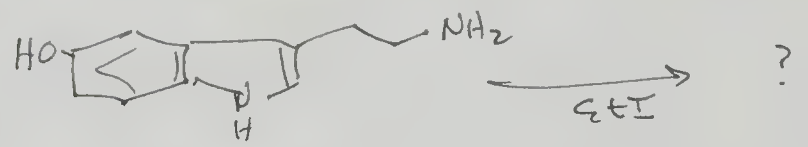








(156) again - try anh!



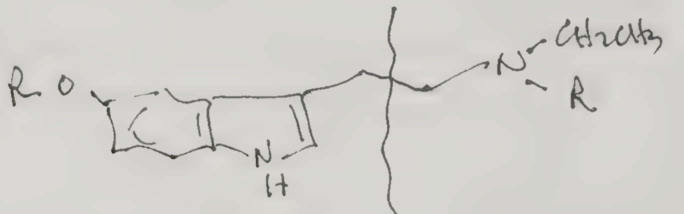
2.12 g serotonin HCl - into 20 ml anh. DMF under Xe
goes totally into solution !!!
10 mM. → add 20 mM. [structure] at 129
x2 2.60
den. 0.742
= 3.504 mL

4.0 ml diisopropylethylamine
looks a bit turbid at
end of addition - then clear

2.0 g (1 mL) EtI - stir.

(½ hr) → Sample out at 0.5 hr. squirt. + 5x H₂O clear
+ drop of NaOH (cloudy!) xtrt 90/10 Sm19 A S1A.
weird big thing, MS ≡ major peak 105
trace of 5-HO-DET ?

(3 hrs) → work up - slightly warm from stirrer. Into 100 mL
H₂O (is sl. basic) - extract directly as is with
3x 40 ml CH_2Cl_2 (some color into xtrt) - pool -
extract 2x 50 ml dil HCl, make aq. basic c̄
ammonium hydroxide - xtrt 2x 50 mL CH_2Cl_2
pool - flash → CH_2Cl_2 off quickly - ~~some~~ much
residue (iPr_2NEt?) off more slowly →
final residue of ~ 1 g - no ~~smell~~ ! so is OK
GCMS in 90/10 Sm19 A S2A. AWFUL One lousy
peak - no spectrum - search for 58 & 86 → nothing.

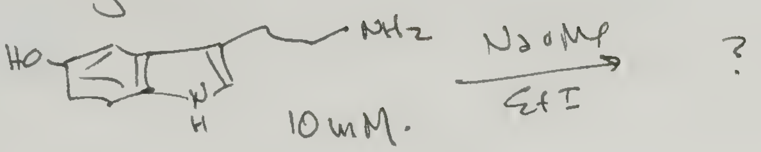


R = H (146) R = H (58)
R = Et (174) R = Et (86)

∴ MW's to look for

H	H	204
Et	H	232
H	Et	232
Et	Et	260

again - try MeONa anh.



10 mM.

2.12 g serotonin HCl - into MeOH 10 ml sol !!

1.1 g NaOMe (20+ mM) then 1.08 - in MeOH 10 mL sol with exotherm

under argon - add MeONa soln to serotonin c̄ swirling - white solids out which do not redissolve (NaCl?). Strip well on rotary.

Residue - bubbly - heavy oily stuff - some solids around the periphery. not nice. Add 0.81 mL (1.56 g) EtI - in 10 ml CH_3CN

Gum, on scraping → goes superficially (surface) white xtals (NaI?) scrape, scratch - more and more xtals. Beautiful. let stand under xenon for a couple of hours. White solids !.

Suspend in 100 ml H_2O (clear) (pH ~10) acidify c̄ dil (1N) HCl → red. wash c̄ 2 x 50 mL CH_2Cl_2 — basic c̄ 5% NaOH - xtrct c̄ 2 x 50 CH_2Cl_2 - some little bit of the brown color does go into the dichlor. pool - flash → small amt - viscous oil.

GCMS page 158

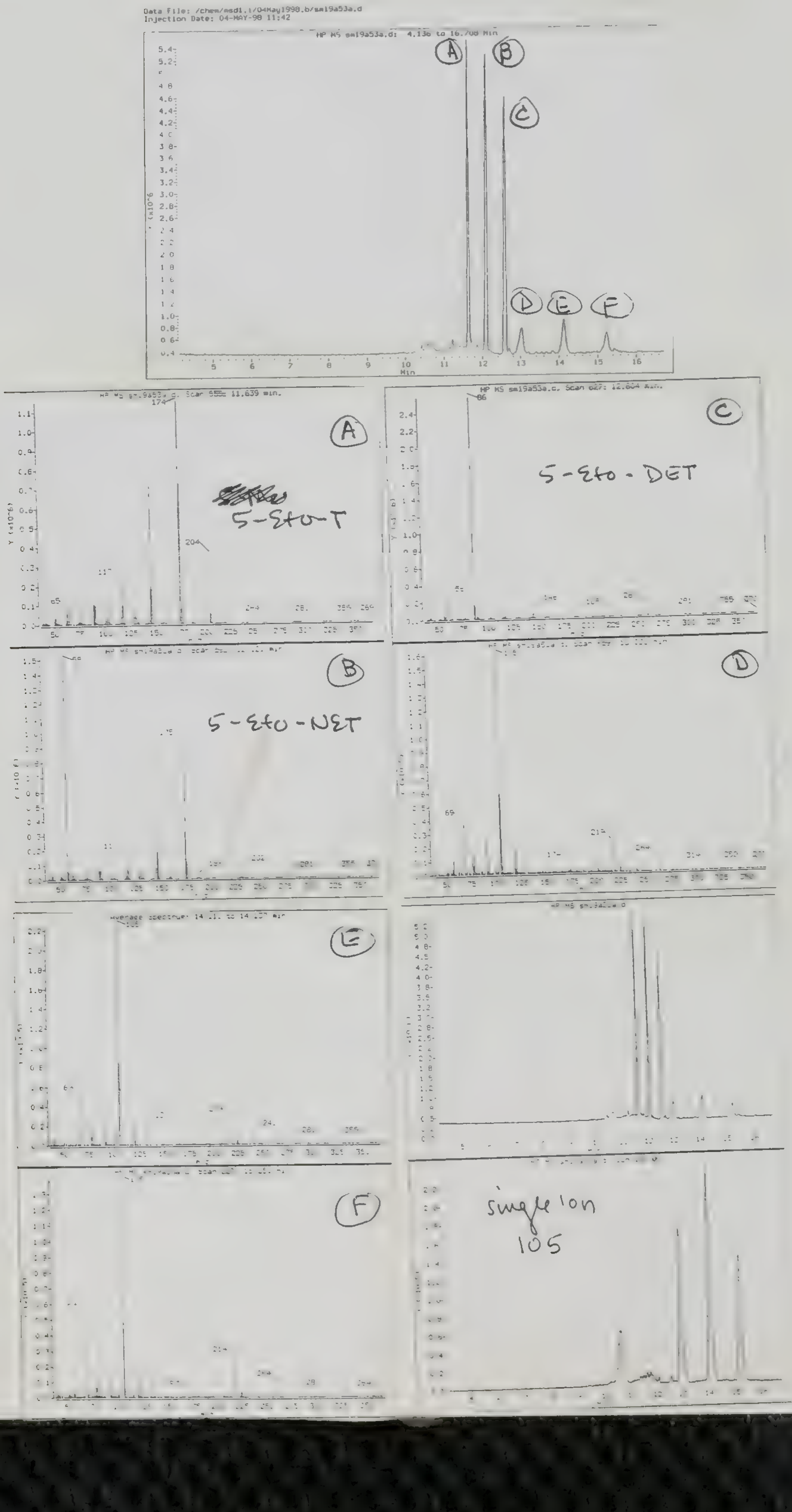
~ = amts 5-EtO-T
5-EtO-NET
5-EtO-DET

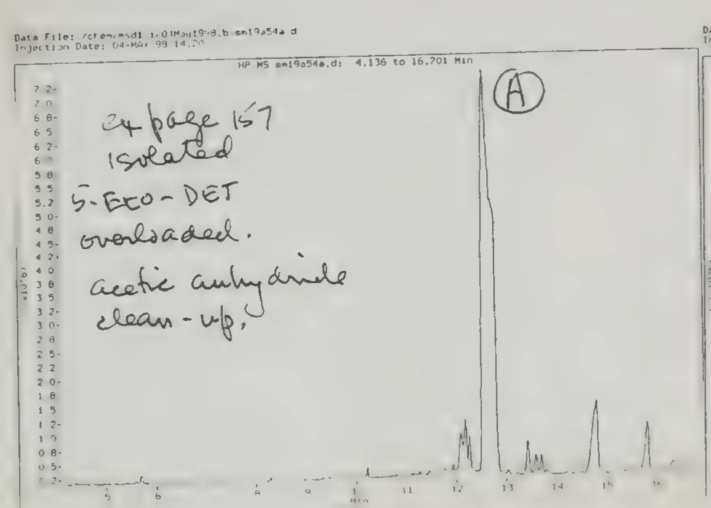
Heat c̄ acetic anhydride
kill NH4OH - xtrct CH_2Cl_2 2 x 25
xtrct c̄ dil HCl 2 x 25 → neutrals - CH_2Cl_2 washed c̄ H_2O - flash → 80 mg neutrals spectra page 160

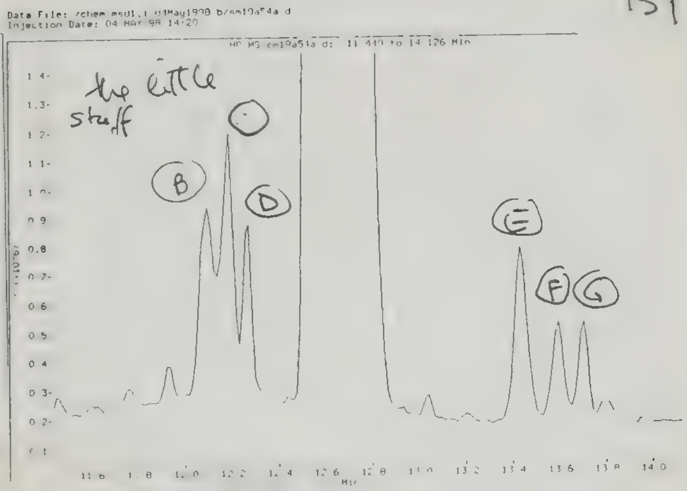
aq. make basic
xtrct c̄ 2x 25 ml CH_2Cl_2
flash → 80 mg

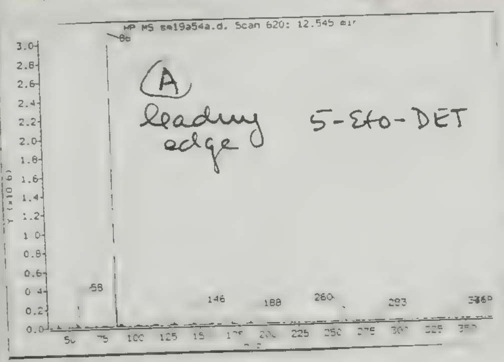
test amine fraction (IPA HCl ether no xtals)
spectra 159

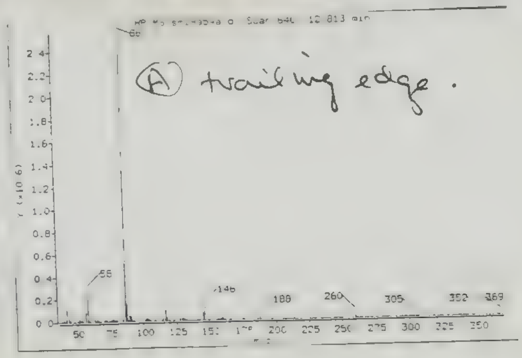
(158) Spectra from 157 5-HT, MeONa, EtI

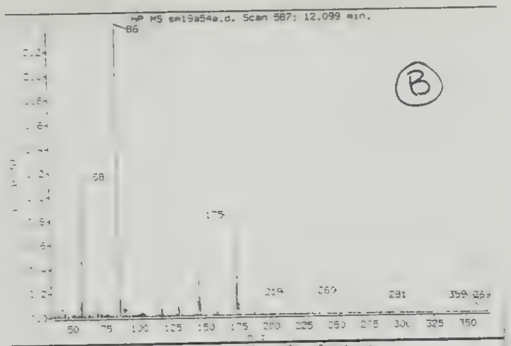


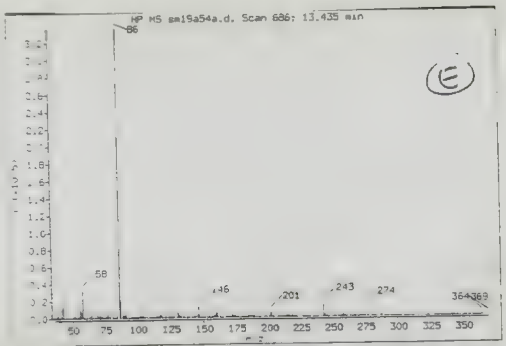

Data File: /chem/msd1.1-01May1998.b/sm19a54a.d
Injection Date: 04-Mar-99 14:20
HP MS sm19a54a.d: 4.136 to 16.701 Min
(A)
c+ page 157
isolated
5-EtO-DET
overloaded.
acetic anhydride
clean-up.

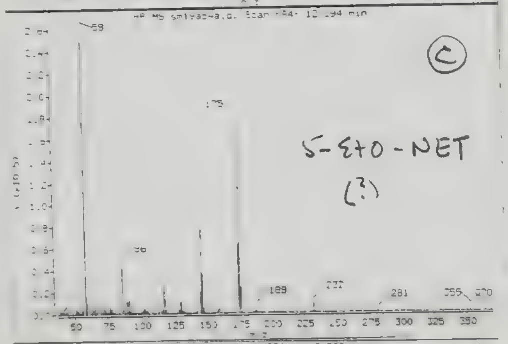

Data File: /chem/msd1.1-01May1998.b/sm19a54a.d
Injection Date: 04-Mar-99 14:20
the little
stuff
(B)
(C)
(D)
(E)
(F)
(G)

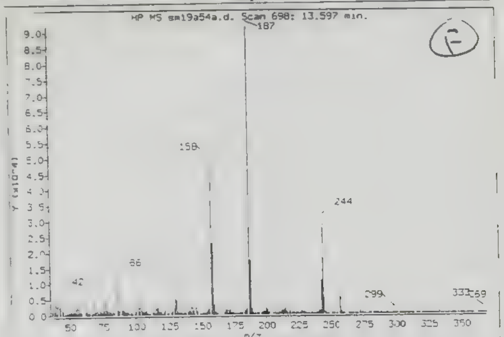

HP MS sm19a54a.d. Scan 620: 12.545 min
(A)
leading
edge
5-EtO-DET

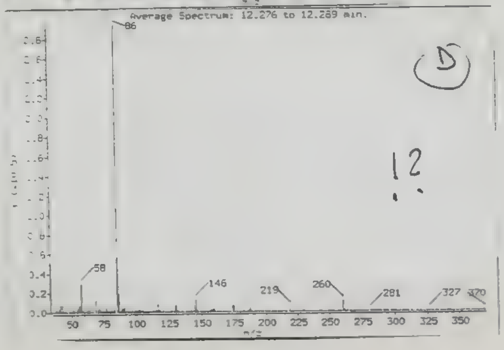

Scan 640: 12.813 min
(A) trailing edge.

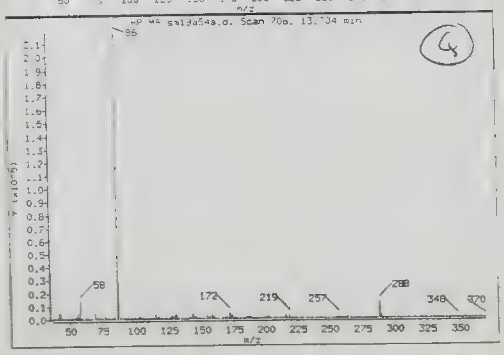

HP MS sm19a54a.d. Scan 587: 12.099 min.
(B)

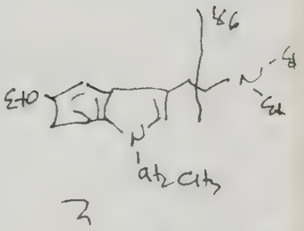

HP MS sm19a54a.d. Scan 686: 13.435 min
(E)


(C)
5-EtO-NET
(?)


HP MS sm19a54a.d. Scan 698: 13.597 min.
(F)


Average Spectrum: 12.276 to 12.289 min.
(D)
!?

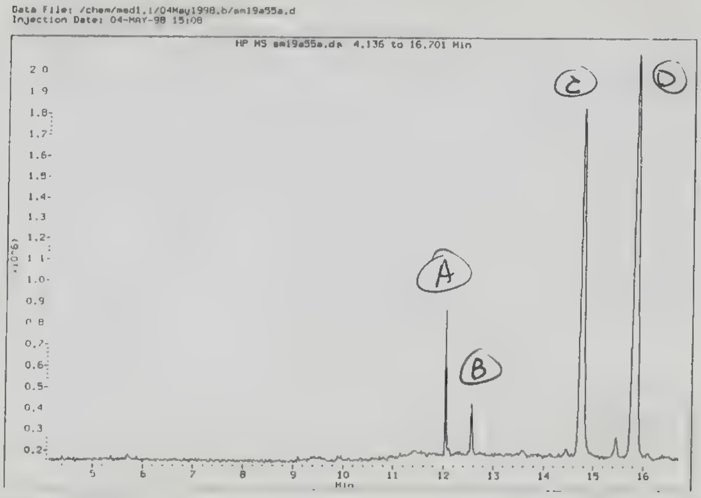

(G)

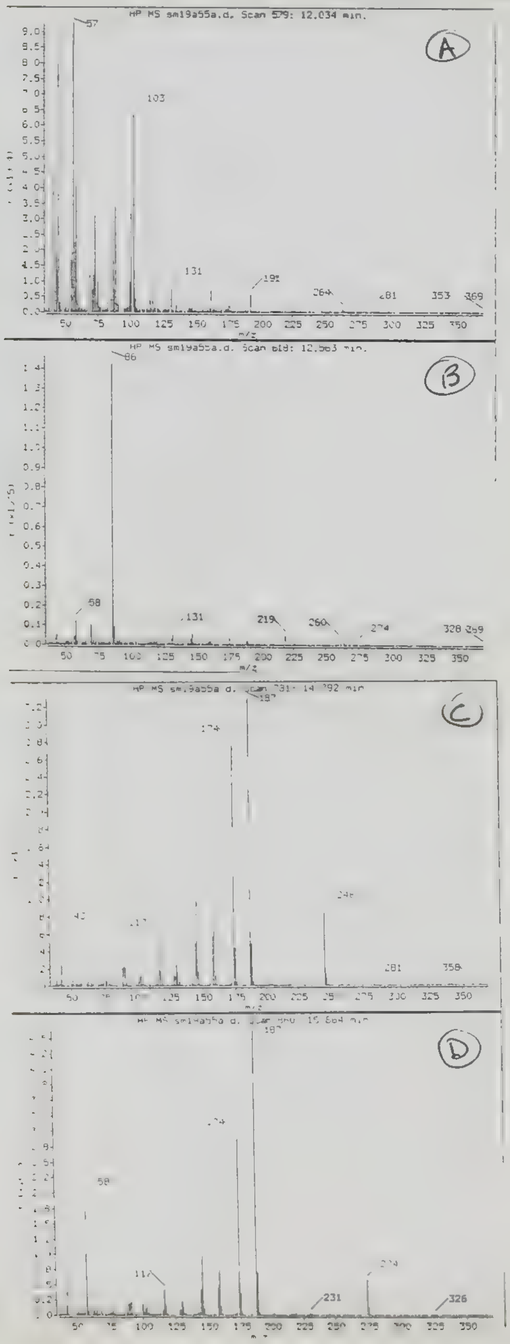

86
EtO

?

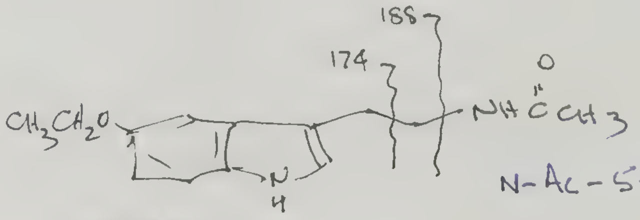
MW 288

acetylated neutrals - ex page 157



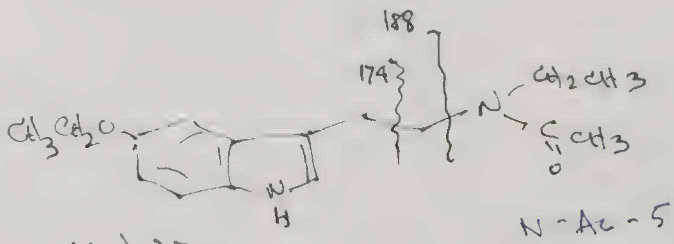


5-EtO-DET



N-Ac-5-EtO-T

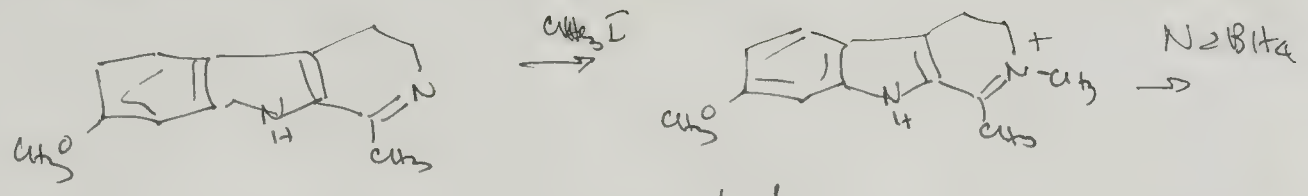
MW 246



N-Ac-5-EtO-NET

MW 274

Small scale exploring

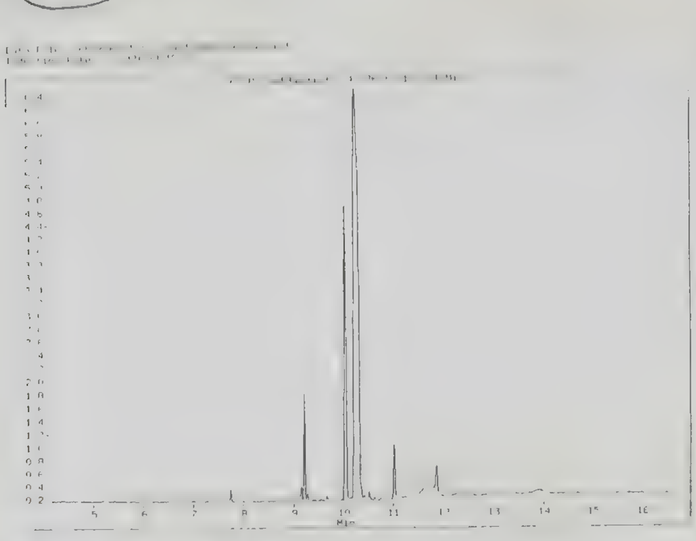


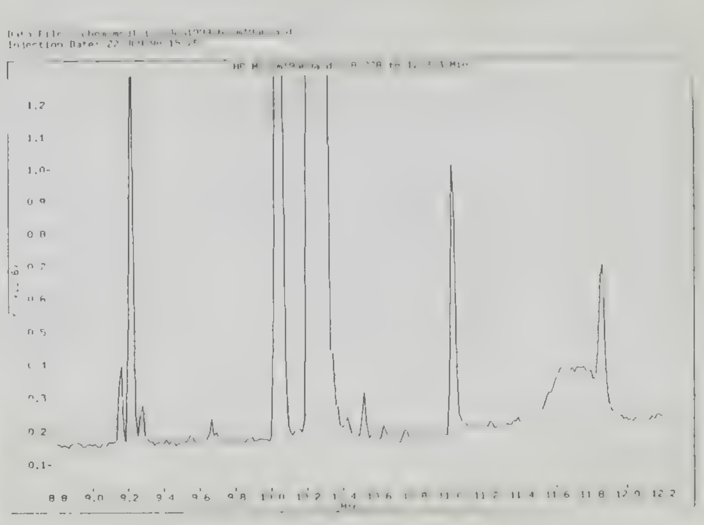
a few mg $H_2 \cdot HCl$ – into water ~1 ml → clear yellow soln. –
add a few drops N NaOH → white cloudy – xtrt c̄
~2 ml CH_2Cl_2 – evap → fine beautiful white xtals.
SM19 A63A Sample TLC (A)

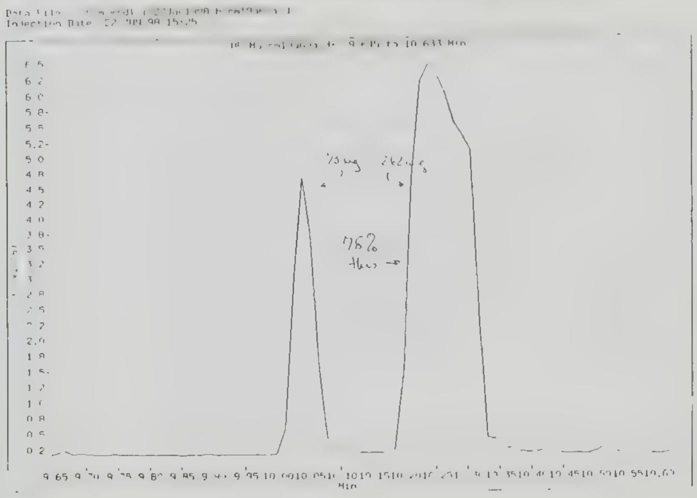
dissolve in ~1 ml CH_3I – never really dissolves but
goes immediately yellow – should have added kinderer
base? Let stand ~3 hrs, CH_3I evaporates
Sample TLC (B)

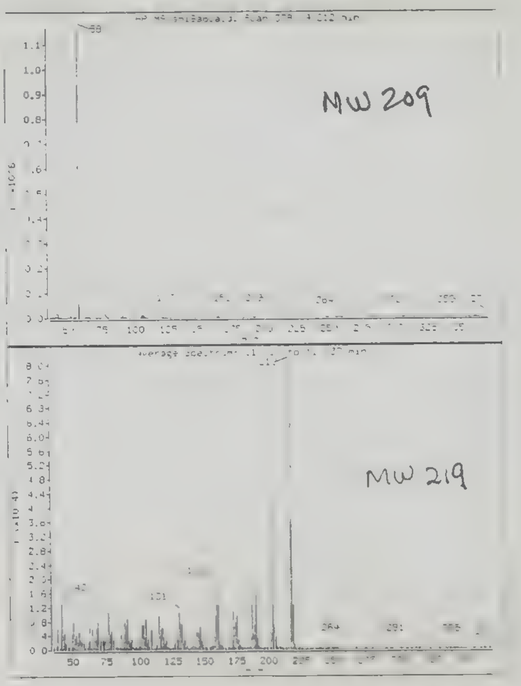
dissolve in H_2O OK, + dil HCl OK → yellow soln –
add two small spatulae of $NaBH_4$ → colorless
but ~~now~~ no white cloudy. xtrt c̄ CH_2Cl_2 – evaporate
→ gummy that on spatula scraping → yellow solids!
see page 164 for harmine/harmaline resolution
Sample TLC (C)
SM19
A64A

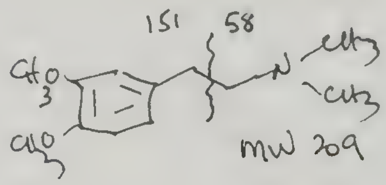
(162) from page 143 incomplete DMMM

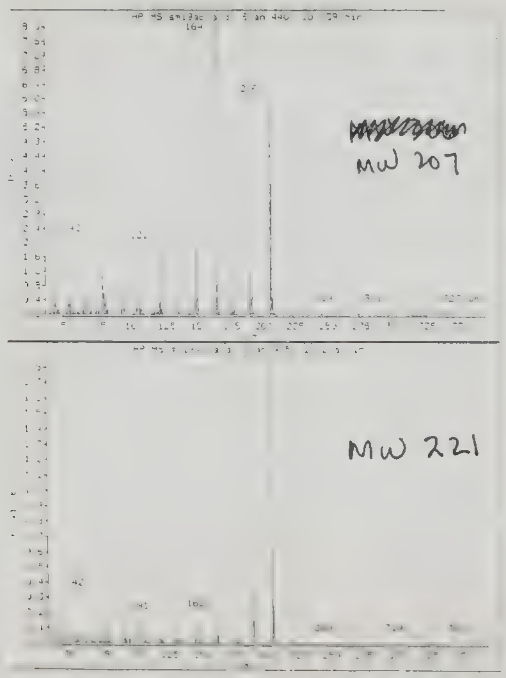


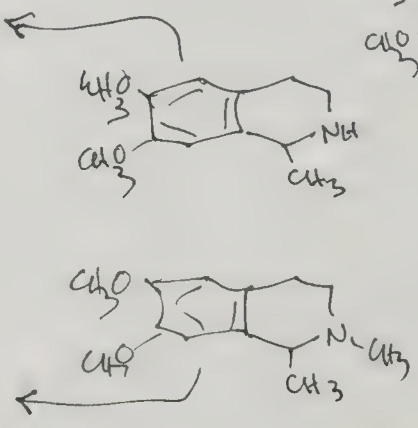




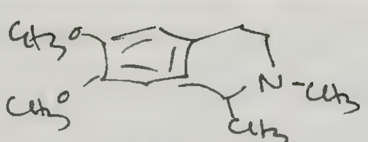








Push the rest of the way.
DMMH → DMMM.



never did push it – used the quat intermediate and that went very smoothly (see page 205)

reanalyzed 143 9 months later – deep brown oil essentially ≡ spectrum

(164) Let's straighten up the Sigma harmaline/harmine where the new Sigma harmaline HCl Lot 123N 123N 3717 appears to be harmine by GCMS page 161

Ref. Harmine

Harmine HCl TCI lot AJ01 I break seal. 10 mg into ~1 ml H_2O (sol) + 5% NaOH - CH_2Cl_2 evap → solid. (A) $M19 A65A A73

Harmine base, p133b - home-made, by oxydation of harmaline (B) A66A

Harmine HCl, Regis - Lot 239 into 1 ml H_2O - + 5% NaOH → cloudy - ext c CH_2Cl_2 - evap → ~ white film (C) A67A

Ref. Harmaline

Harmaline (base?) Sigma lot 28C-0433 - into CH_2Cl_2 - evap → pale yellow film. (D) A68A

Harmaline (base?) Aldrich lot # 01321AV I break the seal! into CH_2Cl_2 (sol) and evap → yellow (pale) film solid. (E) A69A

Harmaline (base?) Aldrich lot # 11226PX into CH_2Cl_2 - flash → film of solid. (F) A70A

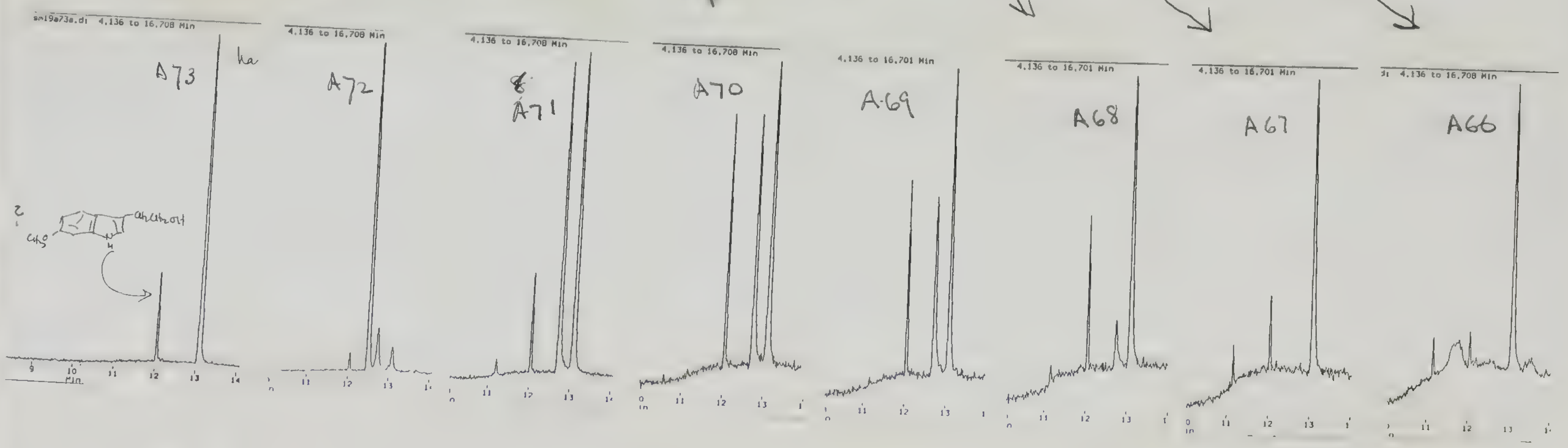
Harmaline HCl Sigma lot #123H3717 - this is the (SUSPECT) sample that precipitated this whole thing. sol in 1 ml H_2O basic c 5% NaOH (G) A71A

Ref. Tetrahydroharmine

Leptoflorine (base?) Regis lot #L549 PL-70 into CH_2Cl_2 - evap. solid film (H) A-72A

A-73A - repeat of A65A -

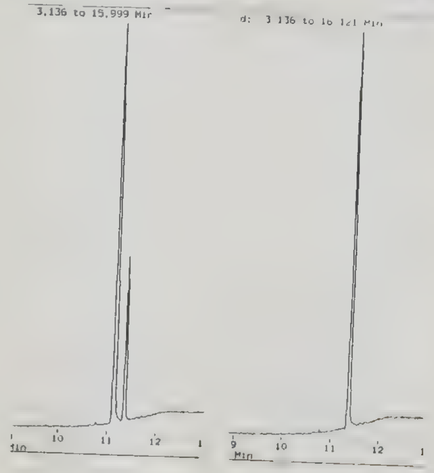
A-74A. yellow oil from Jasmine

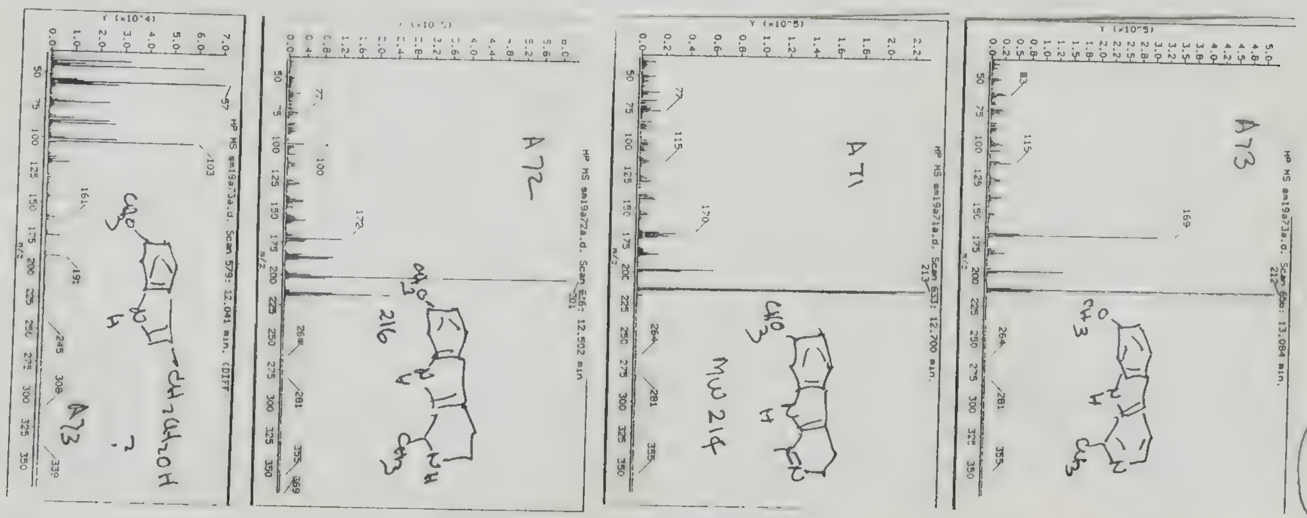


code 127 another harmaline

code 239 -

Same Regis sample clean column



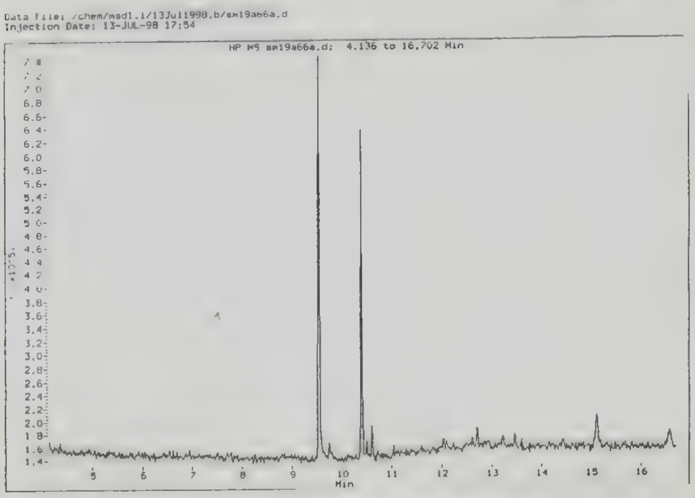


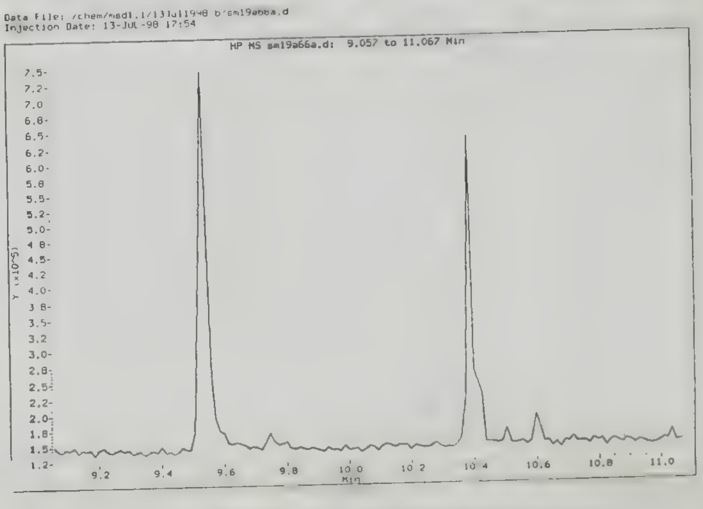
165

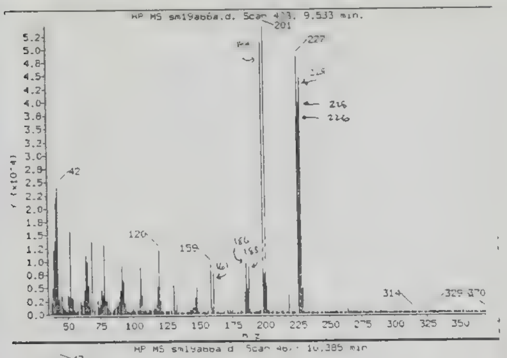
(166) Extract.

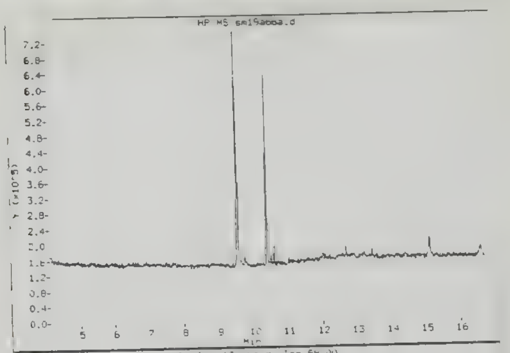
1.8g aerial part

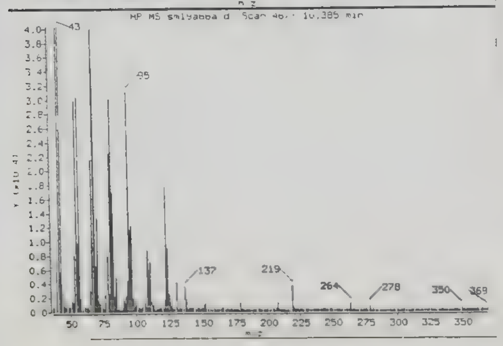
5 ml H₂O – thoroughly smash + squirt 1N NaOH – xtract c̄ 1/2 ml CH_2Cl_2 – 2 phases → beautiful green solution – separate – flash – into ~1/4 ml 90/10

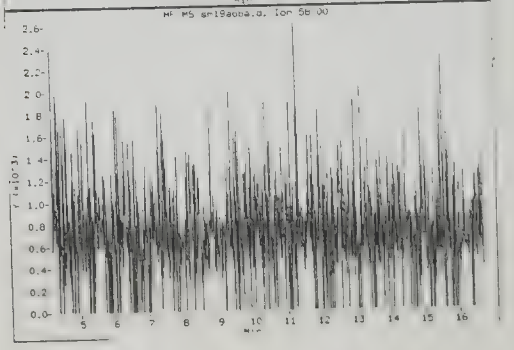


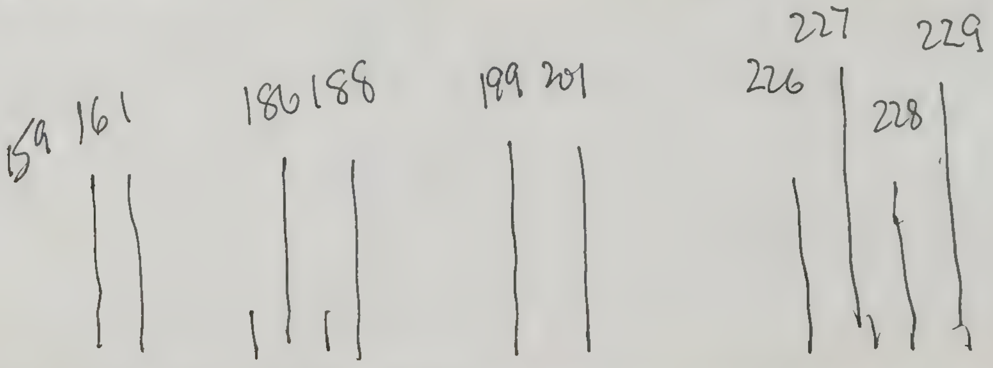


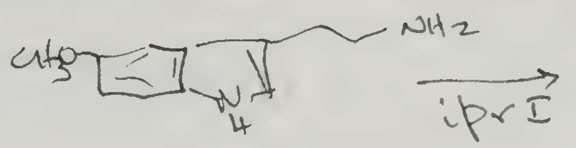






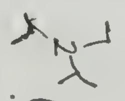






5-MeO-DIPT

|| p121

2.46 g TCI amine - dissolve in
18 g warm (SB) Sulfolane; add
6.5 g  and
9.4 g iPrI TCI

Δ on SB 6hrs. - Stand RT ~ 5 days - 1 φ! why bother to strip on R.E.?

add 150 ml H_2O → 2 φ (heavy oil, red)

xtrt c̄ 35-60° pet ether 3 x 50 ml

heavy strip → 1.16 g deep amber oil. slight base smell

-182.47

-39.77

transfer c̄ CH_2Cl_2 to KR flask 0.92 !?

no smell!
(thank ugh!)

0.2 mm KR!.

95°/40 μ cloudy.

flame-flash into Snorkle. -

up Temp. <155/40 μ. white oil. trivial black pot.

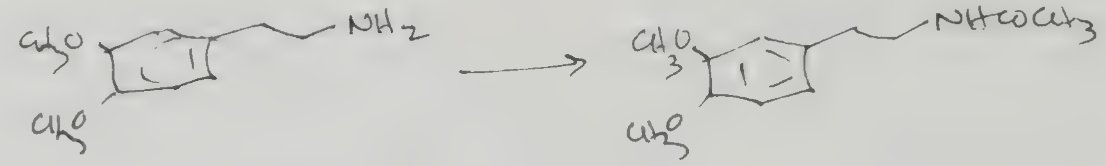
.57 g. 0.57? more? balance crappy

into 2.6 ml IPA
+ conc HCl → red = 23 drops!! xtals
+ another ml IPA (still xtals)
+ diethylether 2.0 ml fine xtals

filter - wash c̄ 10 ml 3/2 IPA/ether → white xtals 0.82 dry?

ML out.

168



11 p 138

9.0 g fresh - clean amine from TCI add
15 ml pyridine add
6 ml Ac_2O - quite hot - let cool to RT over 1 hr
+ 150 ml H_2O - conc HCl → red (a few mL)
xtract c̄ 3 × 75 ml CH_2Cl_2

pool - wash 1 time c̄ 50 ml 5% NaOH. flash.
11.45 g amber oil

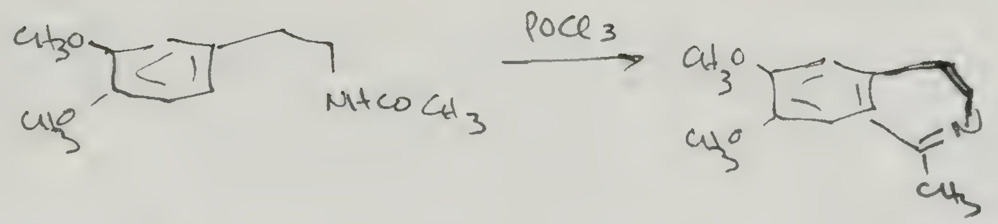
xtals everywhere - trans fer ← I don't trust the balance
to KR pot c̄ CH_2Cl_2 10.58 g solids.

0.15 mm RT KR.
200 μ. 100° melting.
150 μ. 140° nothing.
150° up walls.
150 μ 165° over. white beautiful.
175° ½ over. cool c̄ CH_2Cl_2
180° 10% left. ∇ c̄ CH_2Cl_2
100 μ. 185° done. receiver xtals

Quickals finals
mp (p. 141) 97-98°C ex EtOAc
MS (p. 139) 114 (100%, styrene) 150 (?%) (49%)
149 (23%) 223 7% parent

9.73 in receiver - don't trust balance
9.63 physically removed.
pale yellow solids -
9.50 closer almost white.
to right weight.

0.50 g save
9.00 g to p. 169



|| p144

9.0 g distilled amide - add
42 g fresh, clean $POCl_3$ - onto SB 4:40 P.M.
at ~~first~~ first starts to dissolve - first
heating → some bubbling - hose vent to floor beaker
c̄ H_2O in it - covered c̄ wet towel - no fumes in the lab.
Off in 1-hr. add c̄ great caution to 300 mL H_2O.
extremely exotherm. all in finally -
stand (outside until RT)
xtrt c̄ 3 x 60 mL CH_2Cl_2

evap
(most of the color)
0.14 g
brown
smudge-
OUT

No -
wash c̄ acetone
→ fine white xtal
H_2O sol. CH_2Cl_2
extracted some $\cdot$HCl
(169A)

SM to A28A (sublimed) 1 peak
A29A (xtals) 1 peak
MS in atlas

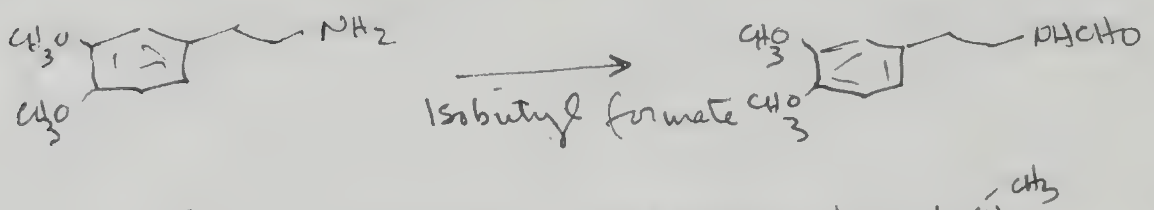
make basic
c̄ 25% NaOH
let cool xtrt c̄ 3 x 60 mL CH_2Cl_2
back-wash c̄ 1 x 50 mL H_2O - flash →

7.27 g cream - solids (169B) sol IPA.

Kugel Rohr'ed 100µ 100°
110° something
130° almost all

main receiver 6.85 g
scrape out, including some from
2nd receiver 6.98 g
Sublimed, largely but some
liquid. (169C)

Sublimed stuff mp 102-106°
(169D) → recrystal ex hexane mp 104-106°
~200 mg in 1 mL IPA ~ 5 drops
(169E) → HCl + 1 mL ether → xtals mp 206-7° dec



9.0 g fresh clean DMPEA. add 20 g $HCOCH_2CH(CH_3)_2$
onto steam bath 5:45 Off in 1 Hr. Add
~ 200 ml H_2O - initially clear, then cloudy.
Conc. HCl → red - xtract c̄ 3×50 ml CH_2Cl_2 - pool -
all color (amber) goes into the dichlor. Wash c̄
50 ml 5% NaOH - almost no color removal.
flash CH_2Cl_2 (some H_2O present, damn it)
→ heavy brown oil - 10.95 g - hint of some acrid
smell. Into KR pot flask c̄ some
dichlor. onto the pump,
Pump for ~ 2 hrs → 100 μ.

130° 250 μ
160° 500 μ losing vacuum
turn heat up

170° 500 μ start
190° 400 μ done - almost colorless oil - that was difficult.

8.70 in main flask

GCMS 164 (100%)
151 (68%)
149 (19%)
209 (15%) parent
165 (12%)

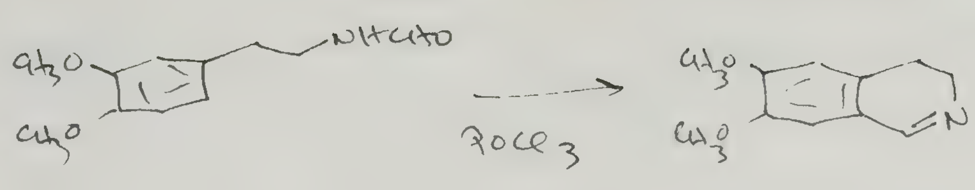
↑ Save as reference ~ 0.5 g
transfer the rest c̄
CH_2Cl_2 for $POCl_3$ p171

call 9.0 g for yield

8.43 (a little stuff was in the 2nd KR flask.

GCMS ~ 95% formamide
~ 5% DMPEA

see page 173
173



8.5 g formamide (CH_2Cl_2 to remove amide from KR receivers - strip on R.E. - add

42 g $POCl_3$ → swirl - exotherm & pretty strong bubbling - outside! - when quiet (and still quite warm) onto S.B. 7 PM off - 1 hr. Stand ON - into ~ 300 ml H_2O - controllable - forgot to ~~wash~~ wash c̄ CH_2Cl_2 - basic c̄ 25% NaOH let cool. - xtract c̄ 3×75 ml CH_2Cl_2 - pool - wash 1 time c̄ 50 mL H_2O - flash → 6.95 g amber oil - smudge on an xtal dish in lab. AM - some xtals (valid, not so I think) + some minor xtals in flask - (not valid - NaCl? - save both.) 6.95 g on questionable balance. Transfer to KR pot - distill. white oil - 135-145°/200 µ -

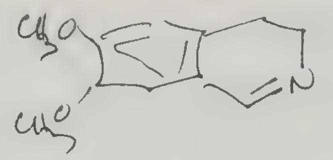
40 µ without setup
100 µ. setup
Δ → ~70°
150 µ.
200 µ 130° over
white
beautiful,
140° a bit left
150° over
say 135-145/200 µ.

6.64 g ← .05 + 6.59 g white oil c̄ some in 2nd receiver.

GCMS
almost entirely
DMHH-2
some DMPEA
see page
173 for
spectra

50 mg.
try seed, doesn't take. 171 A GCMS
a little bit - into IPA + HCl → yellow xtals. wow.
convert all to HCl

strange - on to page 172

(172) play with 

just under 7g of distilled product - colorless when distilled - 2 days later - noticeably discolored. Into 20 ml IPA. - add conc. HCl dropwise - checking acidity c pH paper. - never really red - ~40 drops added - xtals start (yellow). stir - add - 10 ml ether - heavy mass of xtals - (yellowish).

filter.

solids → good quantity of solids. warm c 15 ml 2/1 IPA/ether. IT IS DISSOLVING !!! Suck dry (hygroscopic? no). onto petry dish ~ >3g (172A) for GCMS 2.22g

M. liquors → all ML's → flash. → several mls heavy oil.

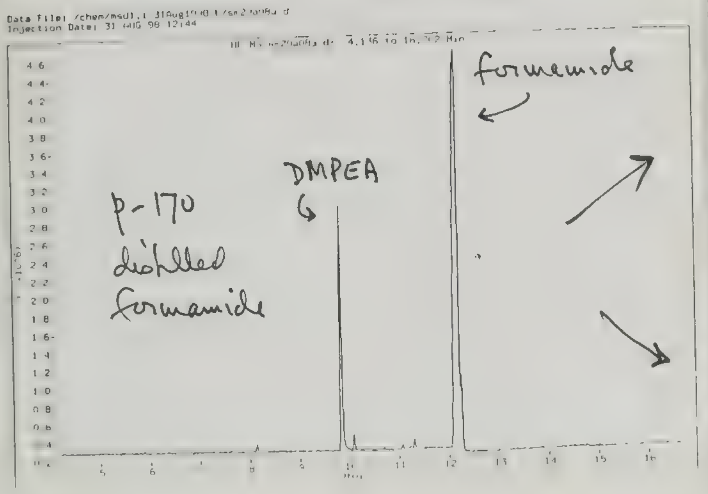
oil into ~100 ml CH_2Cl_2 sol!! xtrt 4 x 75 ml dil HCl → CH_2Cl_2 flash → 50mg of smudge (172B) for GCMS - best OUT. No good. Throw it out. See page 174 & 175

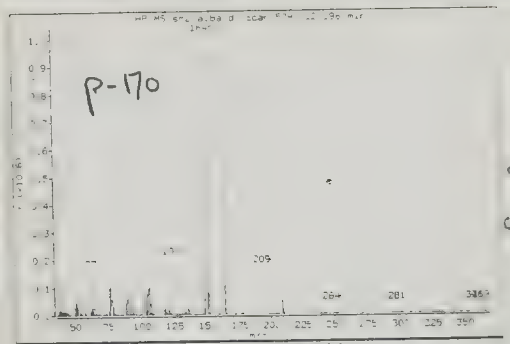
aq. make basic c 25% NaOH xtrt 3 x 50 CH_2Cl_2 - flash → oil fraction 4.47g (172C)

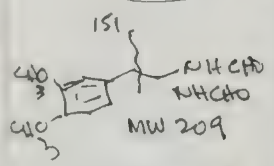
MS 191 (100%) parent 176 (82%) 190 (32%) p-1 133 (25%

→ clean up - add neat 1 ml Ac_2O (hot, becomes thick + 20 ml CH_2Cl_2 - dissolve total ~150 ml CH_2Cl_2; xtrt 3 x 50 ml 1N HCl - wash 1x CH_2Cl_2 - OH: 25% xtrt 3 x 50 CH_2Cl_2 flash → 2.57 amber oil (172D)

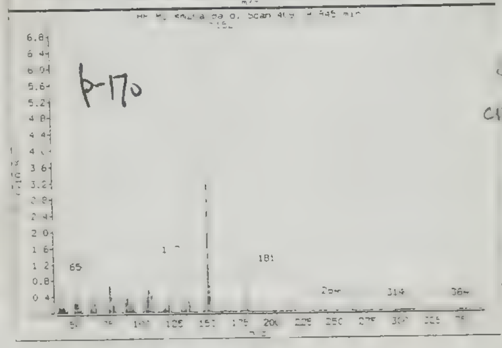
SM20 A25A

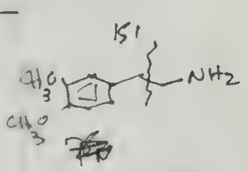




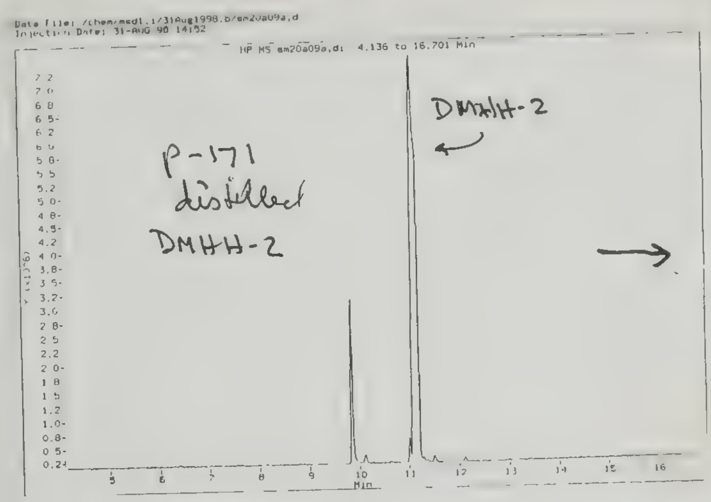


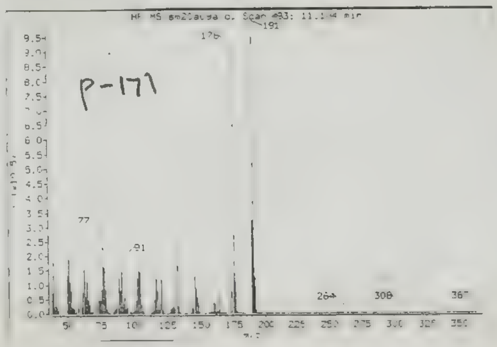
151
MW 209
styrene 164



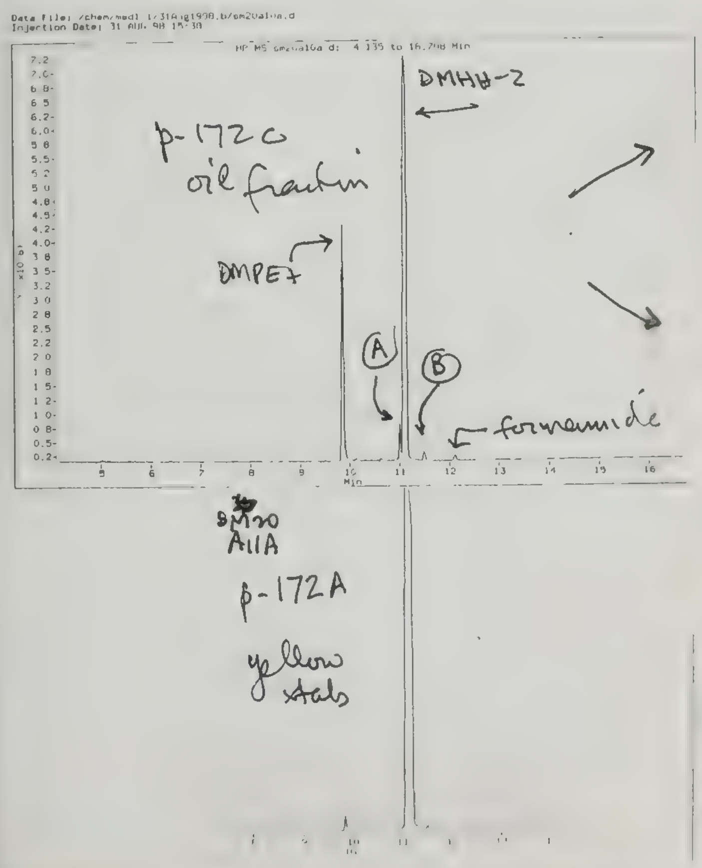


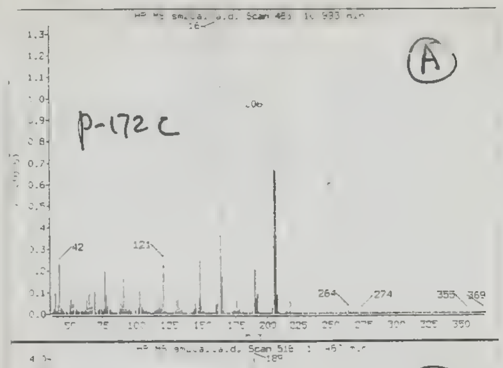
151
DMPEA
MW 181

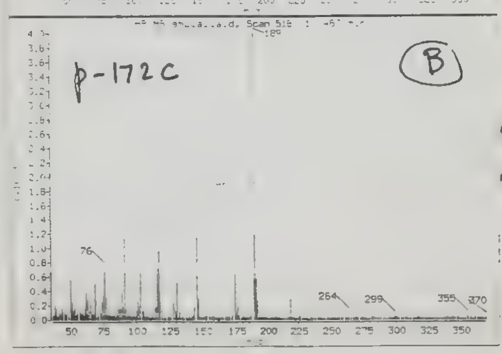


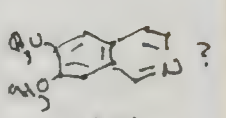


DMHH-2
MW-191

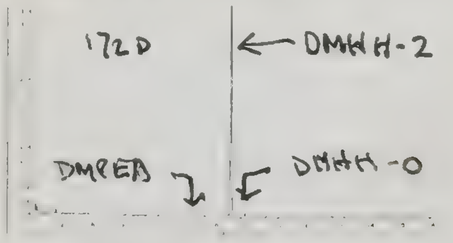






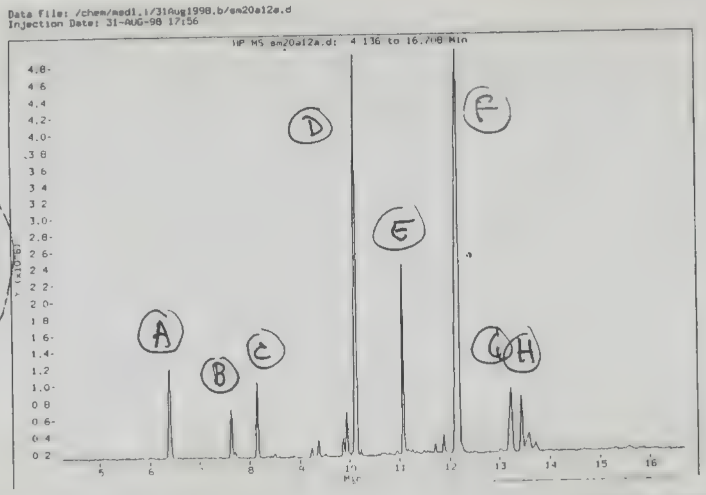


?
MW 189

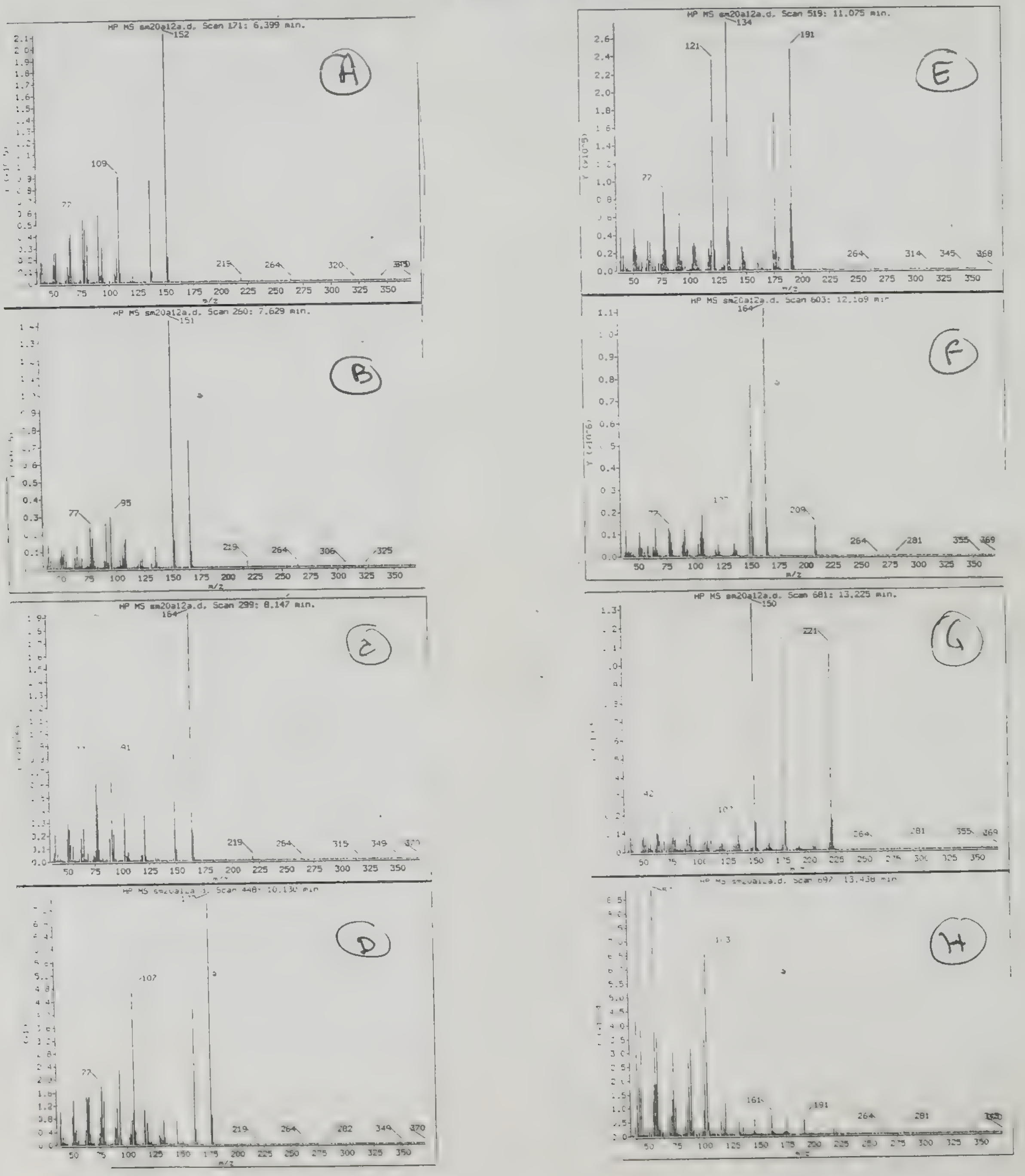


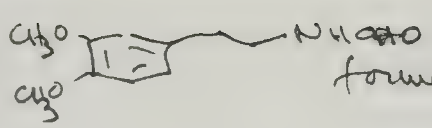
from 172B sludge

Data File: /chem/msd1.i/31Aug1998.b/sm20a12a.d
Injection Date: 31-AUG-98 17:56



neutral or acid fraction →



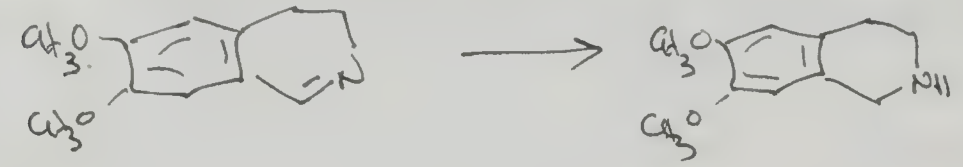
(F) is definitely  formamide

(D) is maybe a zwitterion, ~ neutral

page 172B looks more like 100 mg - deep yellow fluid oil.
lets see if I can get D out of it.

Make extremely strongly basic (hold D as the anion?)
xtrt $\bar{c}$ CH_2Cl_2 (all color goes into org - too bad!)
take aqueous (25% base) + HCl until pH red.
let stand - AM - some colorless xtals -
cubic NaCl! OUT

(176)



DMHH-4

2.55 g DMHH-2 (172-D - presumedly DMPEA free) into ~50 mL H_2O containing maybe 1 mL HOAc. stir - add ~2 g $NaBH_4$ (1/2 in - rather warm - water - cool - 3/4 in add ~1/2 mL more HOAc - add rest. - color never really fades!

Add another 100 mL H_2O, NaOH to pH blue (5%, then 25%). cloudy. xtrt 3 x 50 mL CH_2Cl_2 (some emulsions) wash 1 x 25 mL H_2O. flash → 2.31 g very pale oil to KR.

150 µ.
200 µ 110° no,

~~125~~ - ~~140~~ (mostly to 135) 150 µ. white oil
135 - 145° @ 150 µ 1.80 g - all sets to white solid.

at 180° - sl. cloudy - new - stuff still in pot. Stop rinse out pot - re-KR. at ~ 40 µ. one biddy drop came over at ~ 150° - seed does not take - not worth the gems - OUT, - not out (176-X). for GCMS

Try vextal DMHH-4. hexane no
10% toluene in Hex. no,
Cyclohexane? yes yes. white xtals
{ Keep trace / run GCMS / run IR / run mp. } (176-A) mp 115-127

0.5 g into IPA 5 mL Hot - almost all in. 1 more mL still not all. Δ - no xtals. + conc HCl 6 not enough - 10 drops too much - spont. xtals immediately - filter - IPA wash. air dry → 0.45 g spectacular white xtals (176B) mp 254-256°

see spectra page 178-179

DMHH-4 → DMHM-4

((more or less, 143)) 1.18 g (maybe more?)	DMHH-4 MW 193	~~[illegible]~~ (6.2 mM)	mis-calculated.
into 1.6 mL ~~HoAc~~ in 30 ml MeOH		(~30 mM)	
add 0.5 mL CH_2O 37%		(~6 mM)	
add. 1.5 g $NaBH_4$ exothermic fizzle everywhere.		(~30 mM)	

——— supplement ——— (I miscalculated MW's)

+ 3.2 g HoAc
+ 1.0 ml CH_2O another 12 ~ mM
+ 1.5 g $NaBH_4$ another ~30 mM

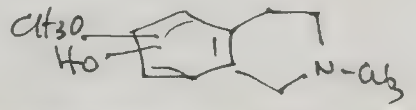
——— supplement. ———

30 ml more MeOH
3 ml CH_2O
4 ml HOAc
2 g $NaBH_4$ good exothermic. (BH_4^- is sl. wet)

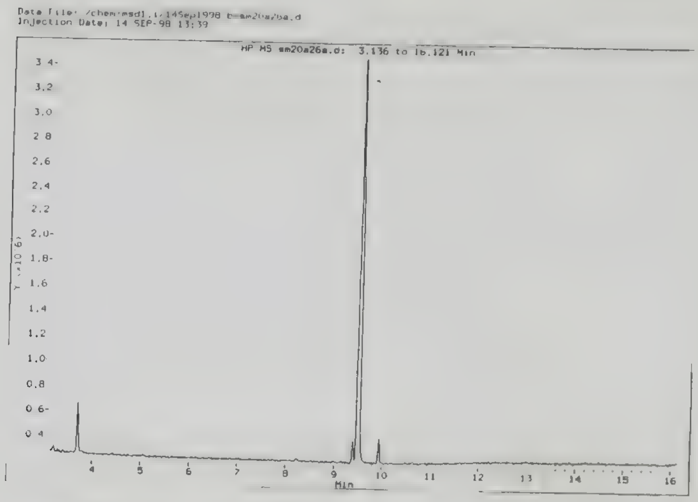
---

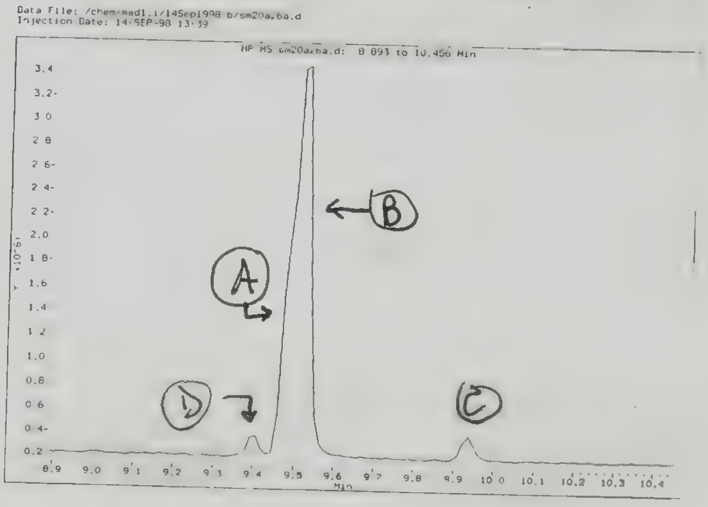
let come to RT. + 300 ml H_2O, NaOH 25% to pH blue
xtract 3 × 50 ml CH_2Cl_2 – flash → 1.53 clear, almost colorless oil. to KR pot. distill.
60 μ.
over 110° –
at 50 μ – first real hard vacuum grease in months!
up to 140 (bp 115-25) and still a bit of fluid colorless in pot. – mostly over. white oil. → 0.94 g

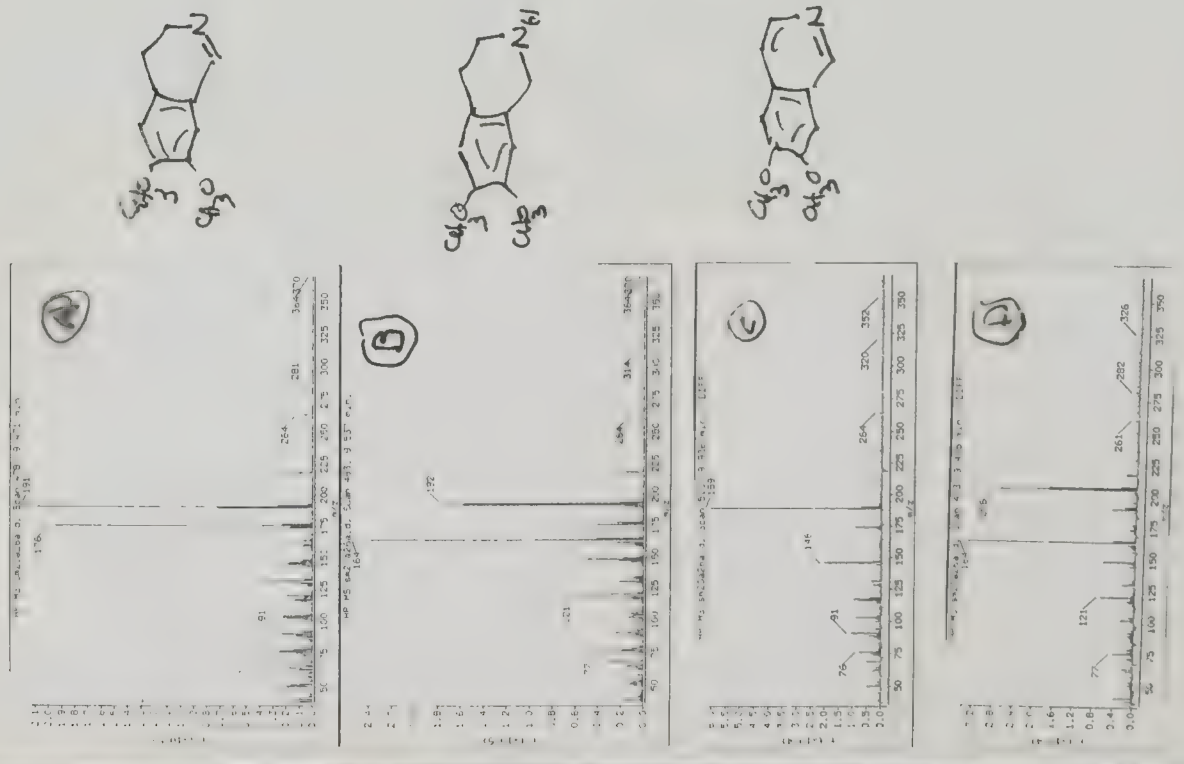
Wrong, wrong, wrong! IR shows it to be a salt, but one that distils! ← (177A)


?

spectra from page 176 DMHH-4

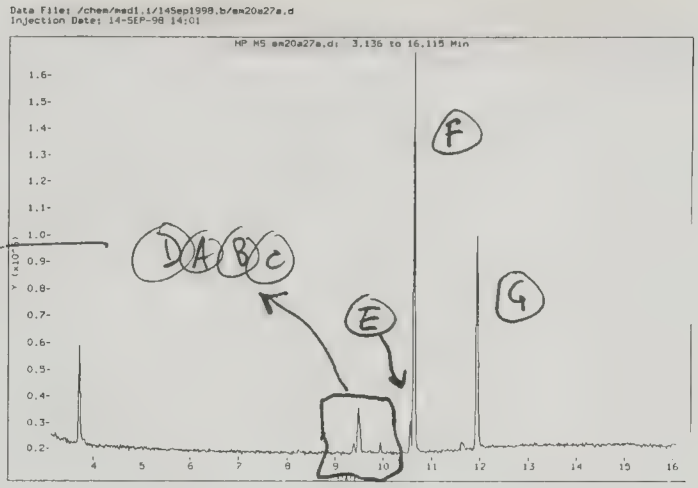




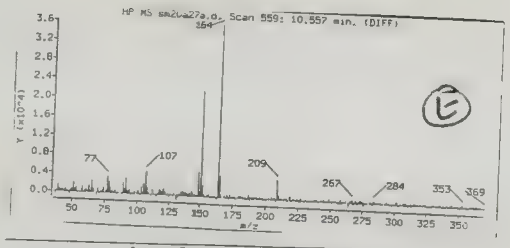


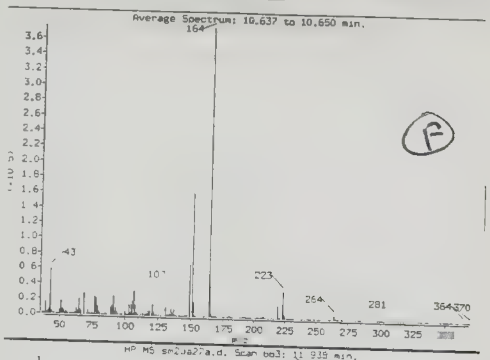
MW 207

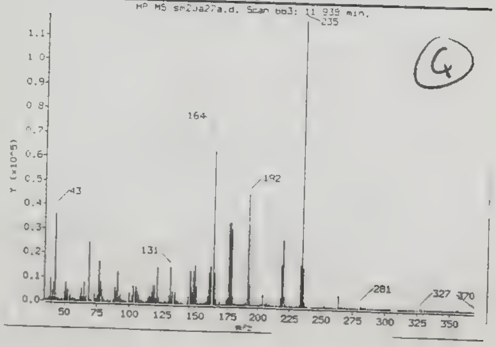
spectra from page 176 re KR (176x) (179)



see these ≡ spectra



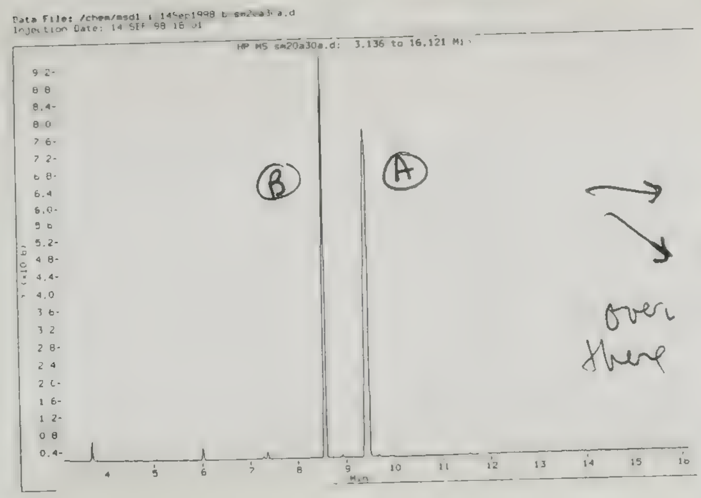


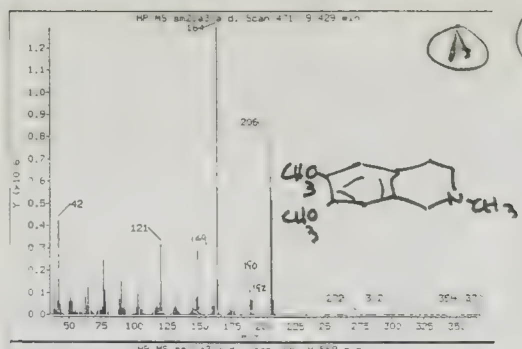


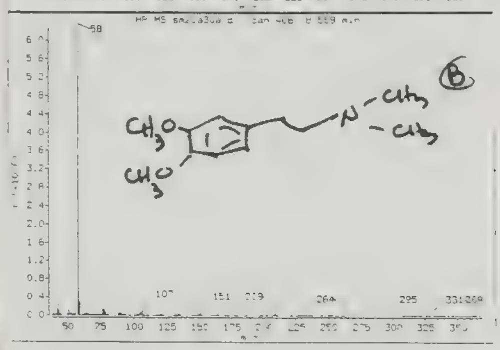
(180) Attempt to methylate "phenolic" product 179.

177A C=17Tox!!!

Data File: /chem/msd1.i/14Sep1998.b/sm20a30a.d
Injection Date: 14-SEP-98 16:?4







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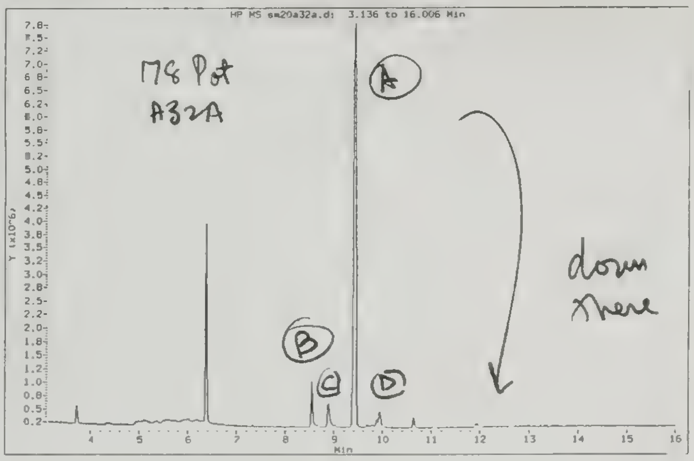

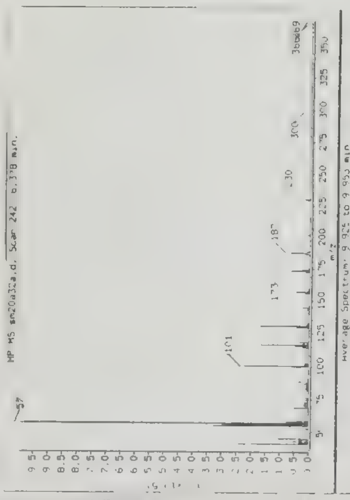

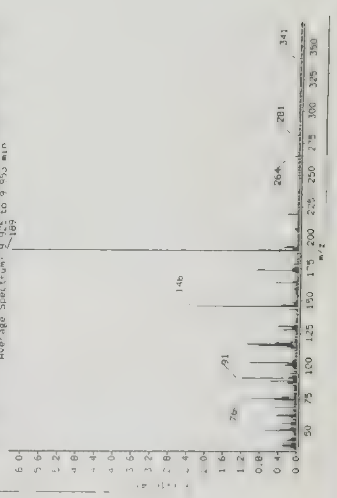

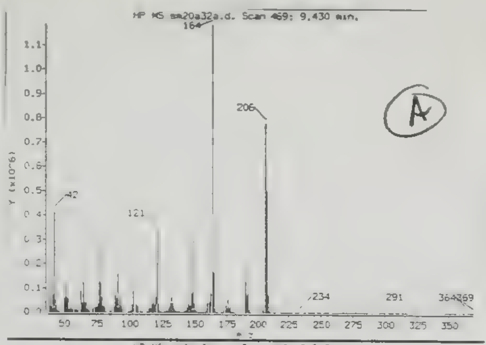

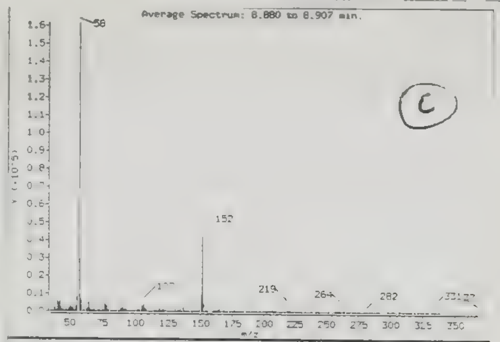

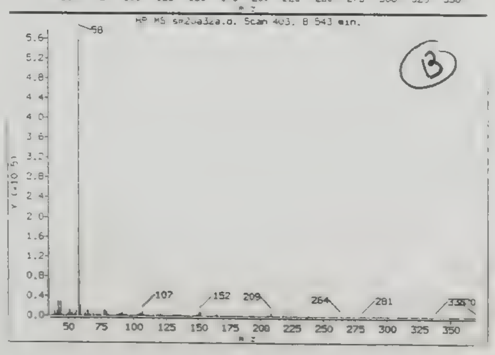

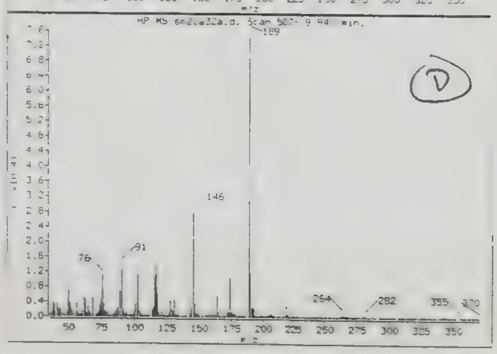

(182)

mono acetylation of 5-HT

→ 2.12 g serotonin . HCl

1.58 g
→ 1.62 ml pyridine - stirrer stops as it goes to a rather solid cake.

→ 1.04 ml Ac_2O added evenly, dropwise, over the surface of the cake - It loosens up to almost a clear solution - and as it stirs more, this begins to thicken. Time ~ 20 min. Add

40 ml H_2O - homogeneous soln. extract 2x 40 ml CH_2Cl_2 flash → 1.7 g thick oil - swells of pyridine - back into CH_2Cl_2 - wash c̄ 1.5 N HCl - flash → 0.9 g white oil ⟶ almost no smell

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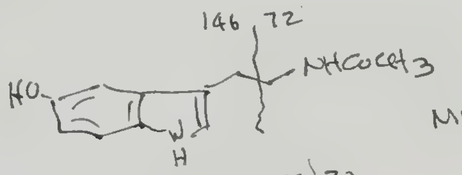
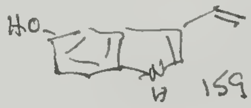
Serotonin 176

N - monoacetyl

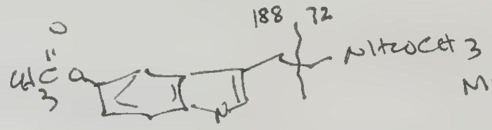


MW 218

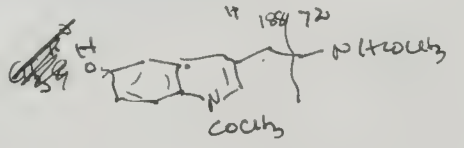


O- Acetyl 188{30
N'- Acetyl

N,O - diacetyl



MW 260



triacetyl

230{72

MW 302

---

take all 0.9 g. Δ in rotary (50°) c̄ a few ML conc NH_4OH - add water - xtrct c̄ CH_2Cl_2. → 0.3 g film. ⟶

"monoacids" (D)

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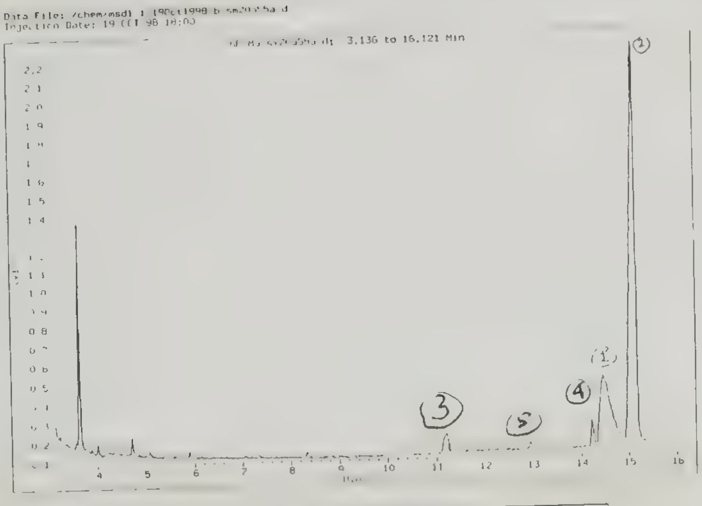
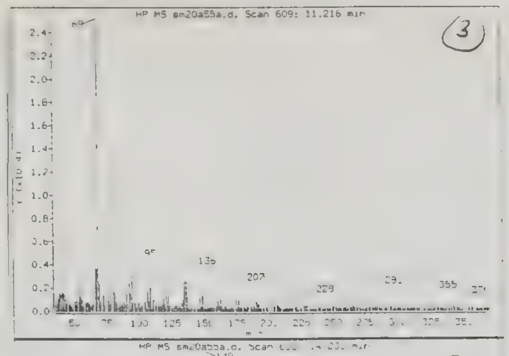
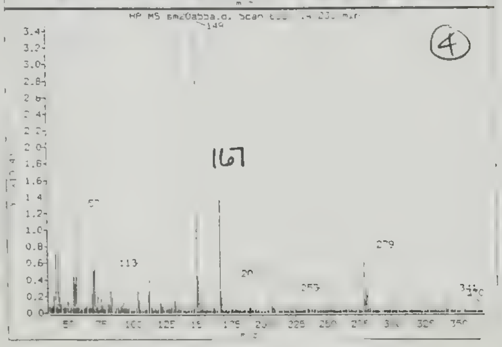
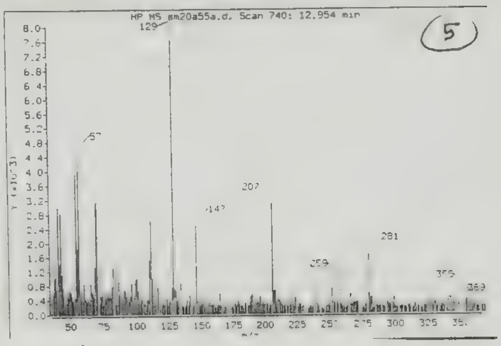
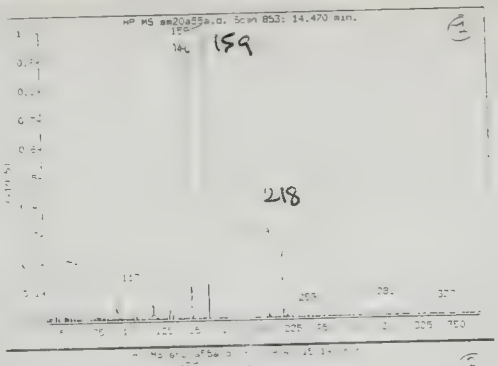
Injection Date: 19-OCT-98 18:0?

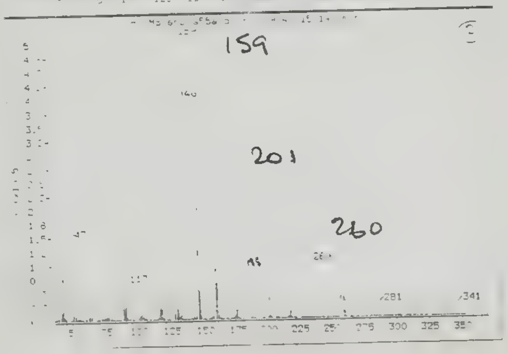












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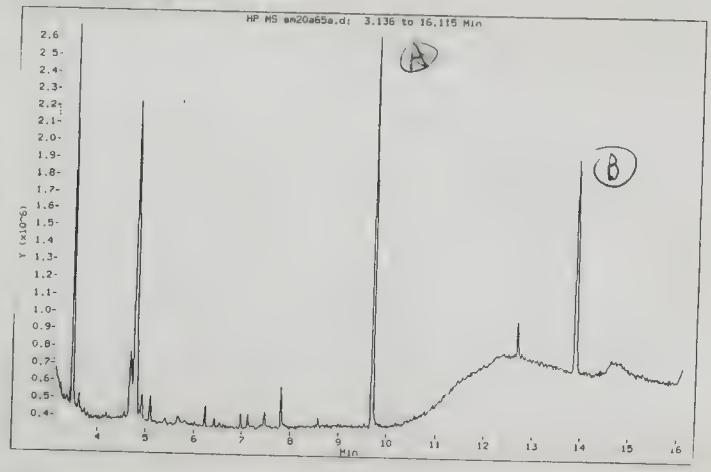
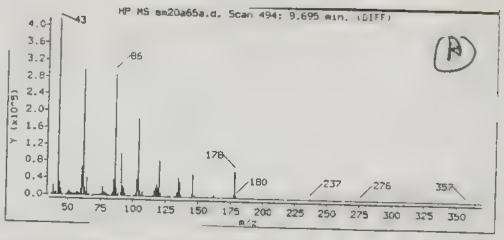
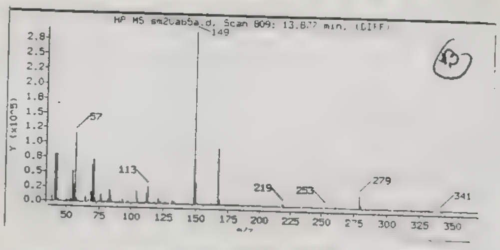
Injection Date: 26-OCT-98 17:12







(184) diacetylation of serotonin

2.12 g 5HT·HCl

3.12 g Ac_2O

~~20~~ 50 ml 6 N NaOH? I don't remember

few drops - into sol.

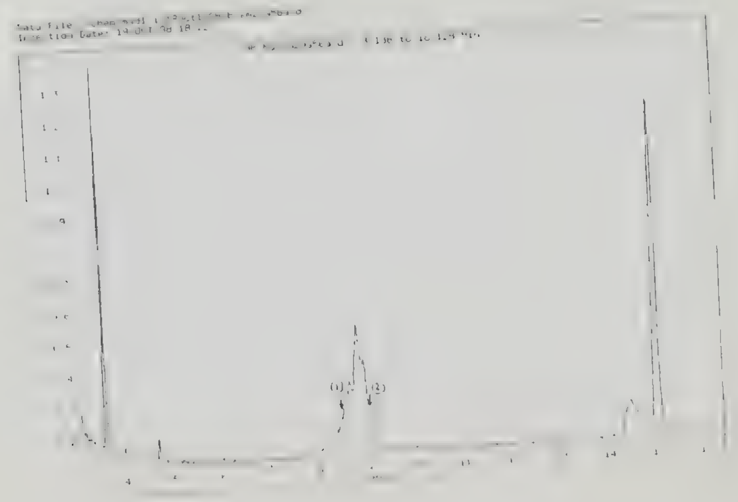
~15 ml cloudy

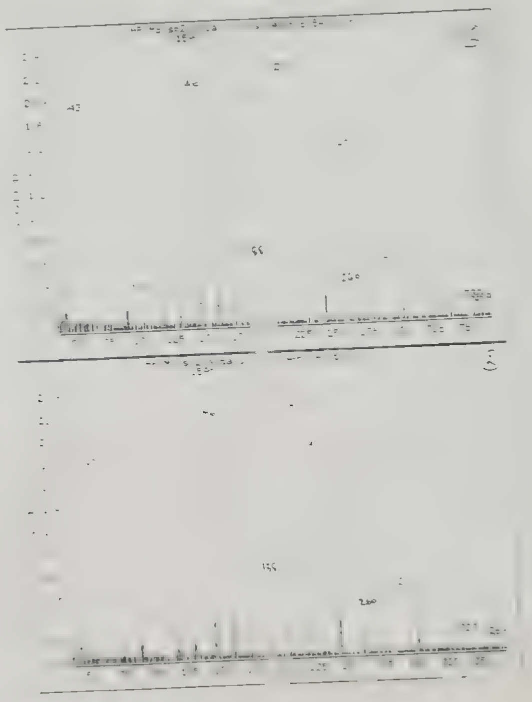
25 ml very cloudy

rest knock out oil phase

xtrt c̄ 50 ml CH_2Cl_2 (must not sol. in either solvent

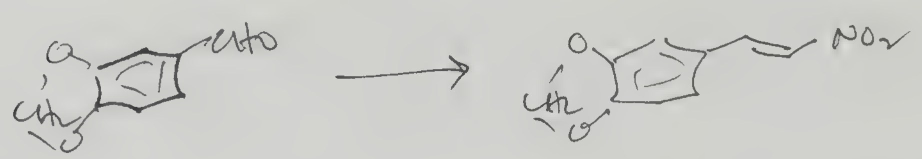
sep CH_2Cl_2 anyway → 2.0 g viscous white oil.





triacetyl serotonin.

(186)



Pinkal
p. 496

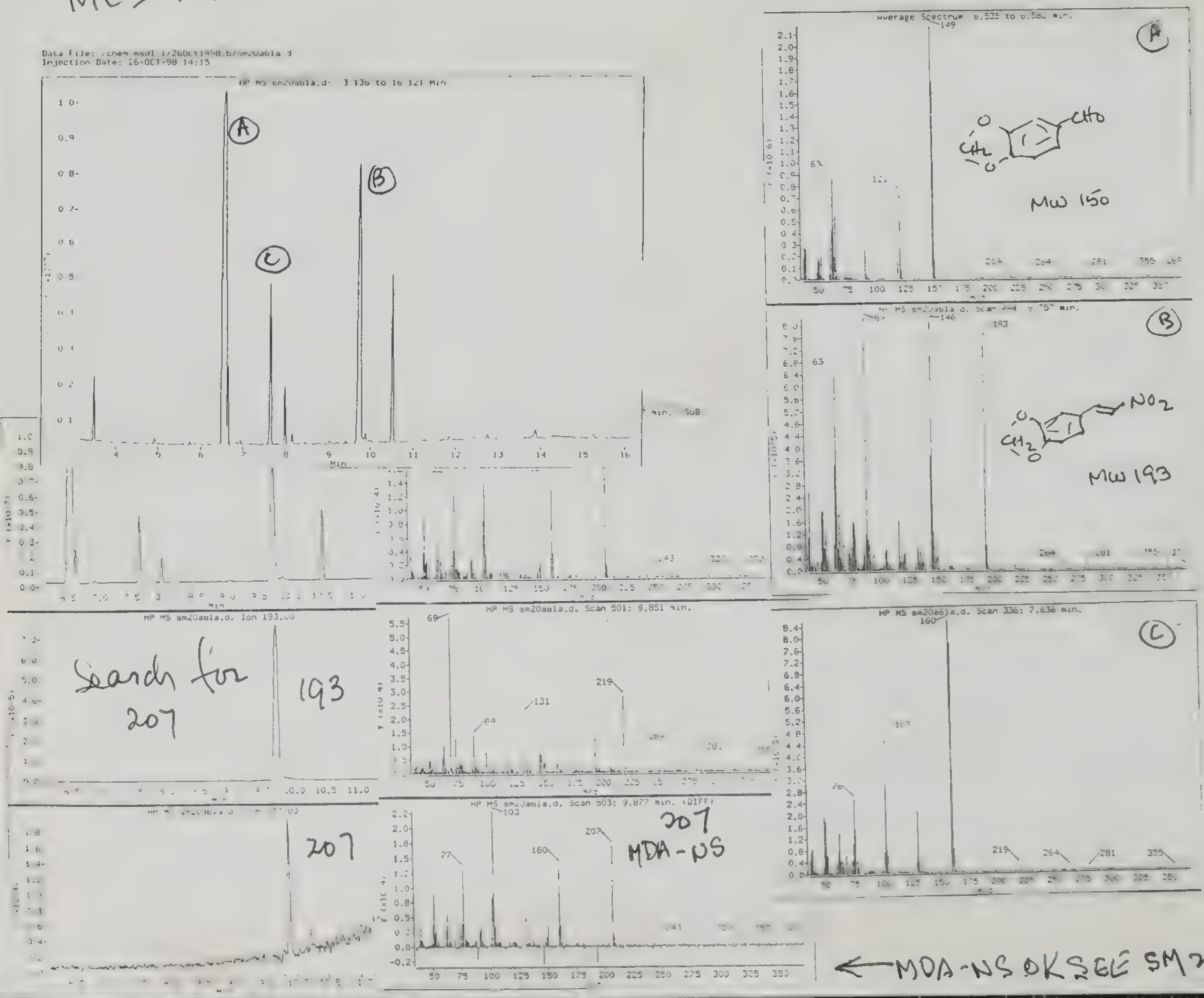
SM20 A61A

30 g piperonal
100 ml HOAc
20 ml CH_3NO_2
10 ml cyclohexylamine (dark brown!)

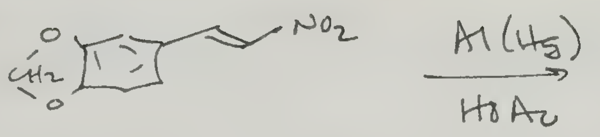
on SB ~ 5 PM — off at ~ 6^{10} — external scratching → yellow xtals

▽ RT. — rather heavy yellow xtals.
filter. wash c̄ HOAc — suck rather dry —
crude wet weight 8.15 g (186A) OUT

ML's stand ON → some more light yellow xtals, (186B) out
ML's + water to turbid — stand → 3.7 g wet (186C) out see repeat p 189



← MDA-NS OK SEE SM20 A96



4.8 g Al foil (~1 foot - 1" squares) +
0.12 g $HgCl_2$ in 180 ml H_2O - let amalgamate -
clearly ready in 30 min
decant off H_2O - wash 2 × 200 ml H_2O
1 × 200 ml IPA.

add 100 ml IPA
\+ 10 ml HOAc (RT)

add 2 g wet NS page 186 in 20 ml hot IPA.
stir - stand ON - AM - grey sludge

filter - wash 150 ml H_2O
150 ml H_2O
20 ml IPA
100 ml H_2O - small white solid-specs - not soluble. ml pale yellow.

~~xtrt 1x 75 ml~~ add 200 ml + ~5 ml conc HCl.
xtrt 1 x 75 ml CH_2Cl_2 - all yellow into org -
strip.
↓
0.52 g sharp smell (HOAc?)
visc yellow oil.
SMA62A

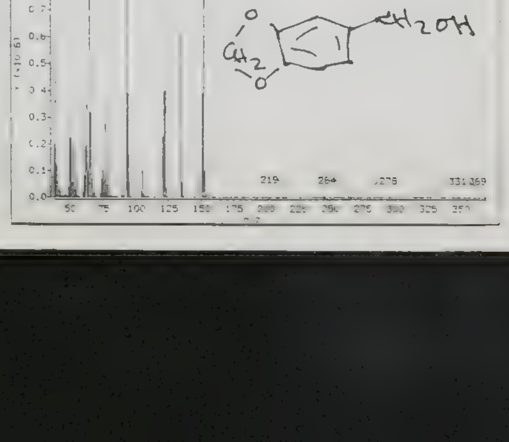
make basic c̄ 5% then 25% NaOH
xtrt c̄ 75 ml CH_2Cl_2 (no color).
strip.
↓ SMA64A
0.40 g viscous white oil.

see next page

neutrals

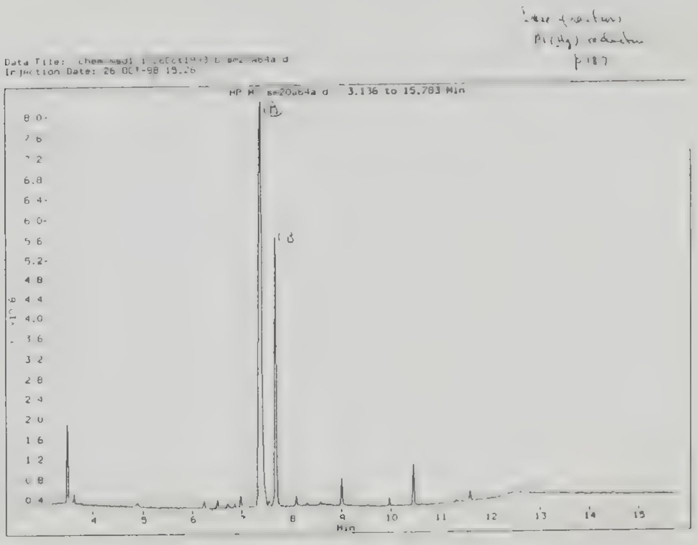
this is pretty good homopiperonylamine

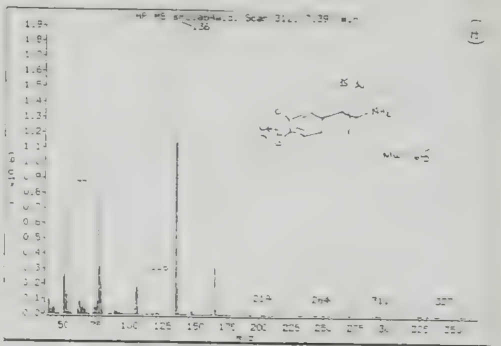
to page 195

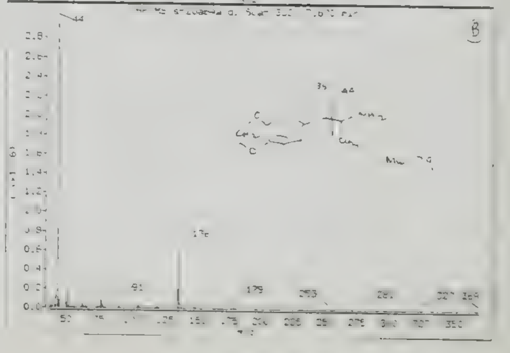


(P.88)

Base fraction from Al(Hg) red. of NS
(page 187)
SM20 A64A.





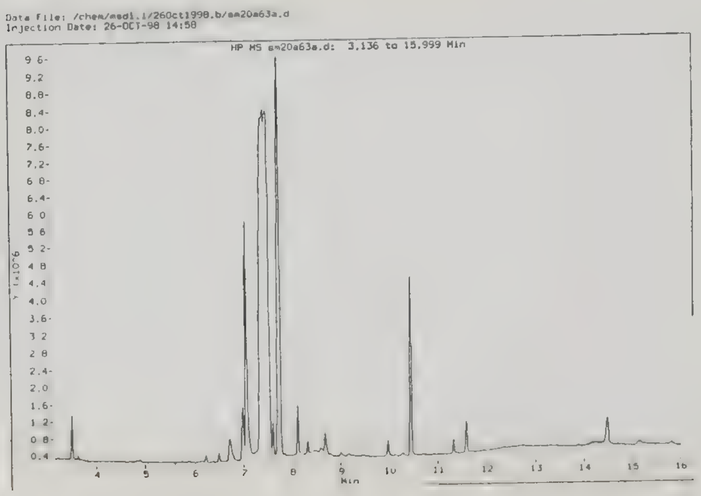


A64A

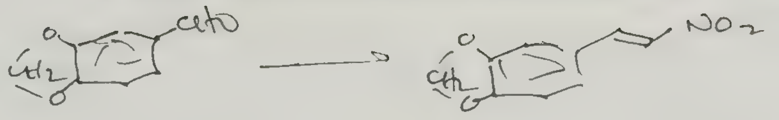
↑ diluted ×10

↓ overload

A63A



Another try:



(189)

|| P. p512 2CD
P. p503 2CB

25 g piperonal
75 ml MeNO2 Aldrich 96% pure
Lot 01109 CT 4 liter

endothermic soln.

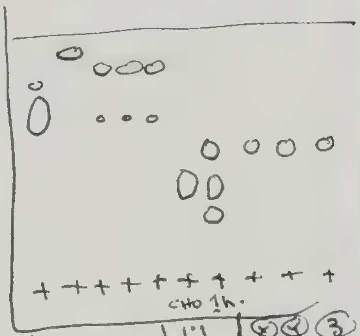
2.5 g anh. NH4OAc - not sol.
colorless - on SB 10 AM.

1 hr. turned a dirty yellow - TLC → short xtals
Rf .6 yellow
Rf .5 aldehyde
Rf .4 ? no color

off at 2 1/4 hrs. - into beaker - ∇ to cold water temp → heavy yellow xtals - filter - wash c̄ RT methanol,
air dry → 16.53 g beautiful yellow xtals
(189A)
Small amt. sol hot HOAc, xtals on ∇,

from ML's + washes -
on standing: more xtals vs NS
filter → (189B)

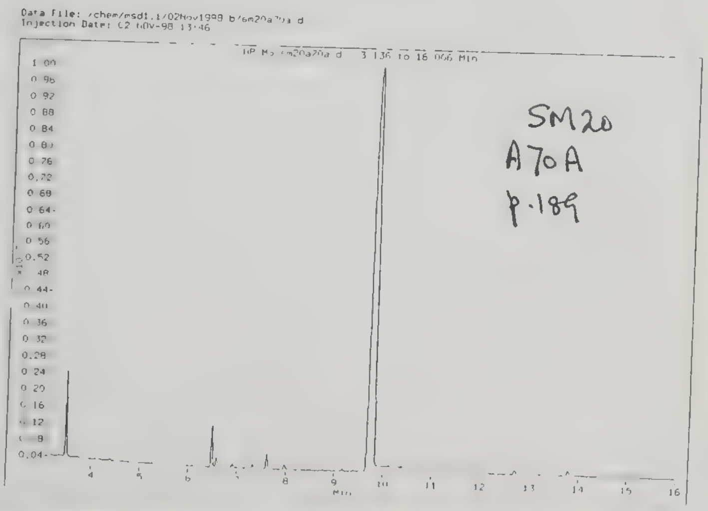
TLC stuff



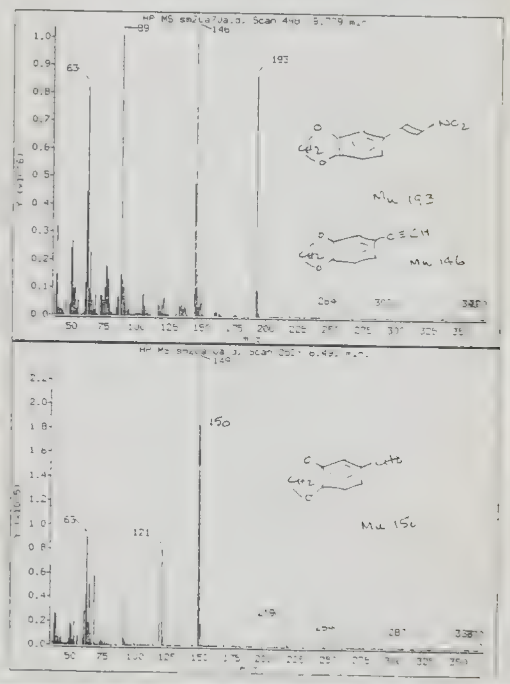
Leitz CH2 - 1:1 CH2Cl2 hex. CHO 1 hr.
CHO NS 186
MDA ABC

play c̄ rextal.
Small amt 186 A
Wash boiling IPA (X)
xtals f. MeOH (Y)
1 1/2 hr pot to RT (Z)

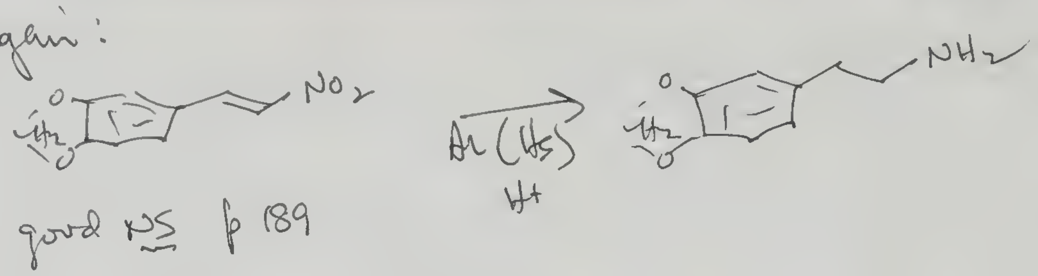
mp stuff.
189 A. 155-8
ex MeOH r158
ex HOAc 161+63



Piperonyl-NS from HOAc



(190) Try again:



Start c̄ good NS p 189

16.3 g good NS, 189A into 200 ml glac. HOAc
~1/2 hr on steam bath needed -
clean soln.

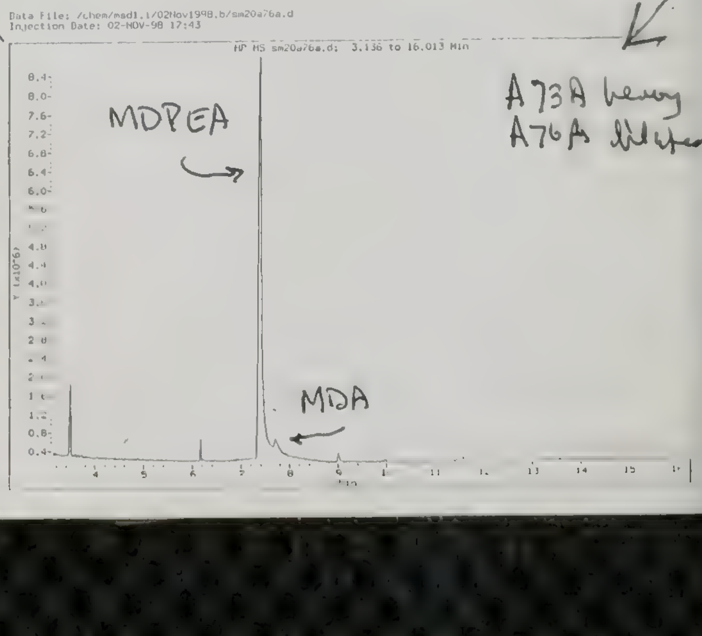
40 g Al foil - 1" squares - amalgamate c̄
10 g $HgCl_2$ in 1.4 L H_2O

1/2 hr - amalgamate taking - probably should have given more time to drain, wash 2 × 1.4 L H_2O, 1 × 1.4 L IPA - drain well - add:

1 liter IPA } - all RT, add:
100 ml HOAc }

NS in hot AcOH. add c̄ pretty good hand stirring -
1st glup - immediate yellow opaque (hot to cold? HOAc to IPA?) add the rest over 5 minutes. stand ON.
AM - clearly the amalgam has been killed - lotsa Al - much color still. Decide not to push - just work it up.
filter all solubles - orange filtrate - wash Al c̄ 3 × lotsa IPA - combine - flash → heavy yellow-red oil c̄ xtals in it. into CH_2Cl_2 - xtrt 3 × 100 ml dilute HCl - pool - back once c̄ CH_2Cl_2 - pale yellow HCl ∅ CH_2Cl_2 → See page 192

OH^- c̄ 25% base - xtrt c̄
3 × 50 ml CH_2Cl_2 - flash → 2.0 c
of base fraction. To KR.



A73A heavy
A76A diluted

0.2 μ
0.15 μ 80° blush
90°-100°/0.1 μ 2.35 white oil
marvelous
picks up CO_2 like a shot.
smudge to GCMS 191
rest to formamide - page 197

detectable MDA - $EtNO_2$ in the $MeNO_2$

Attempt: (191)

(191)

|| to 170

2.3 g freshly distilled homopiperonylamine, rinse out of KR flask c̄

7.0 ml isobutyl formate - Immediate solids !!? Must be a bit of carbonate - very quickly - rest of formate gives no more - ∴ not immediate Rx - no formic and smell in formate. Onto SB 5:30 - Off - 1.25 hrs

into 100 ml H_2O + HCl to pH Red. xht 3 × 50 ml CH_2Cl_2 flash → 3.44 g almost colorless oil - smells of IBuF to KR - 0.05 mm immediately & white solids in pot. Δ 140-160° (tighter) at 40μ → white oil that xtallizes. 2.40) call 145-155° 2.45 g

3.44 smells of IB formate

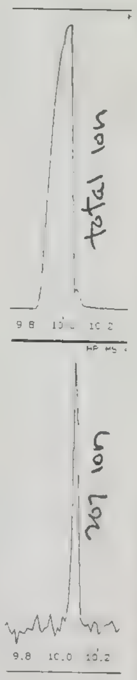
60μ 110° nothing

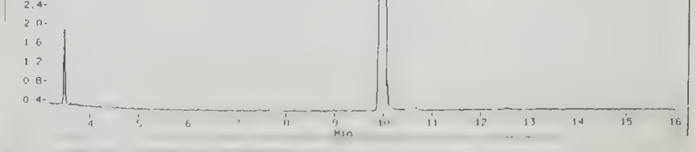
40μ 136°

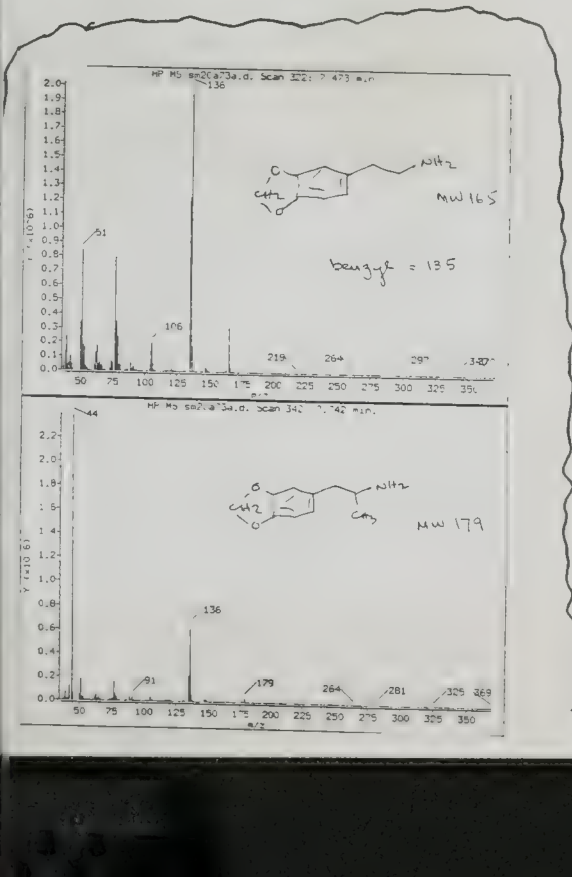
2.45

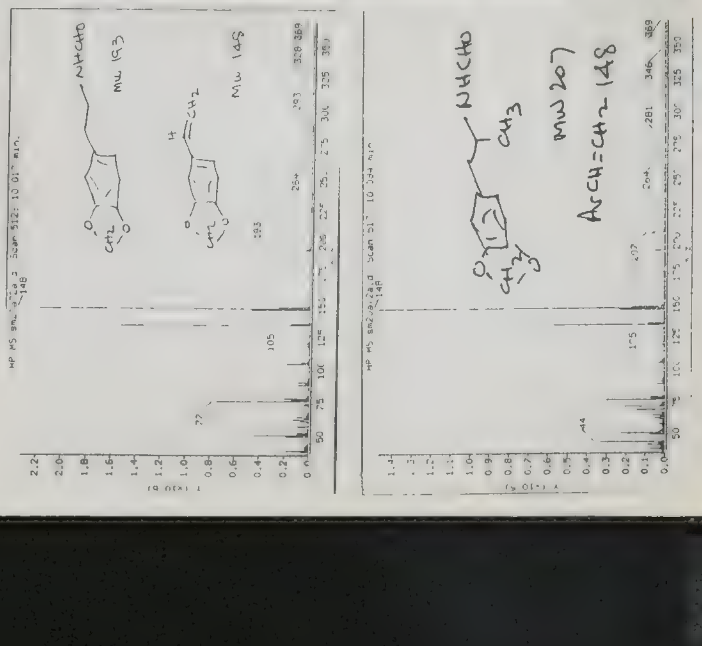
2.40 isolated

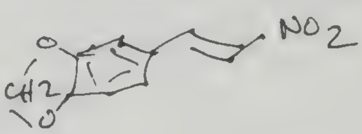
sample p(191) 2.30 on to DIQ.









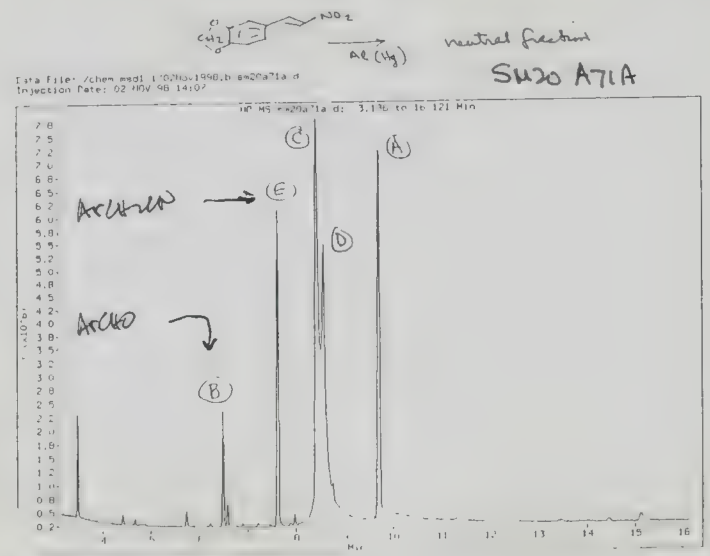
(192) neutrals from  NO_2 $\xrightarrow{Al(Hg)}$

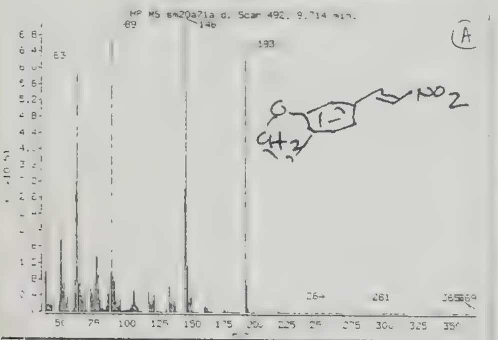
See page 190

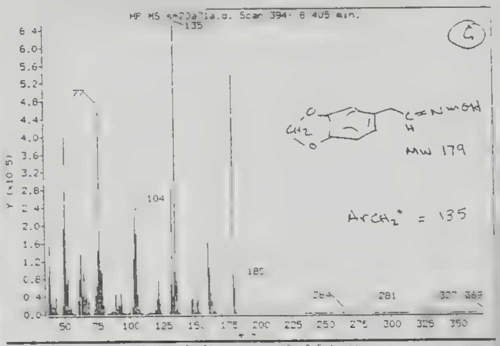
The deep red dichlor phase (HCl extracted) taken to dryness on the R.E. → red crystalline residue (192A) 10,36 g

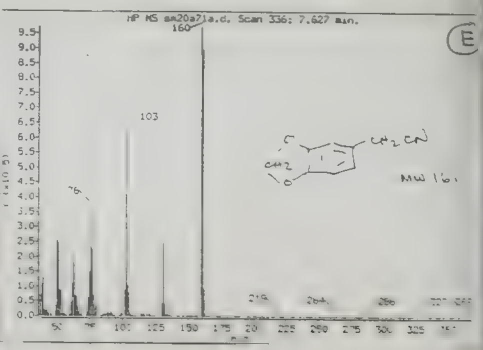
Scrape out 8,7 g

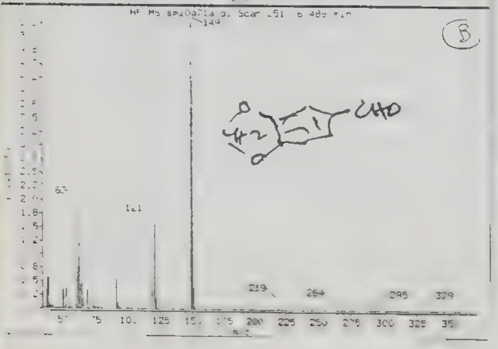
Save in homoveratryl amine area

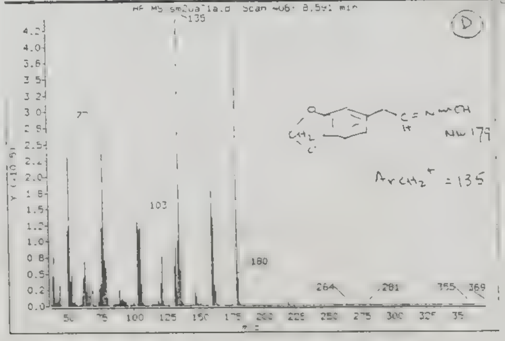


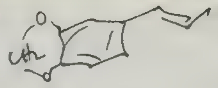




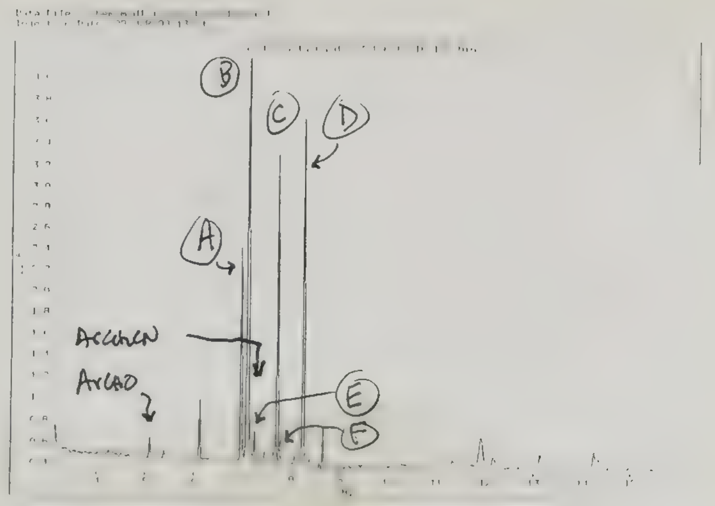


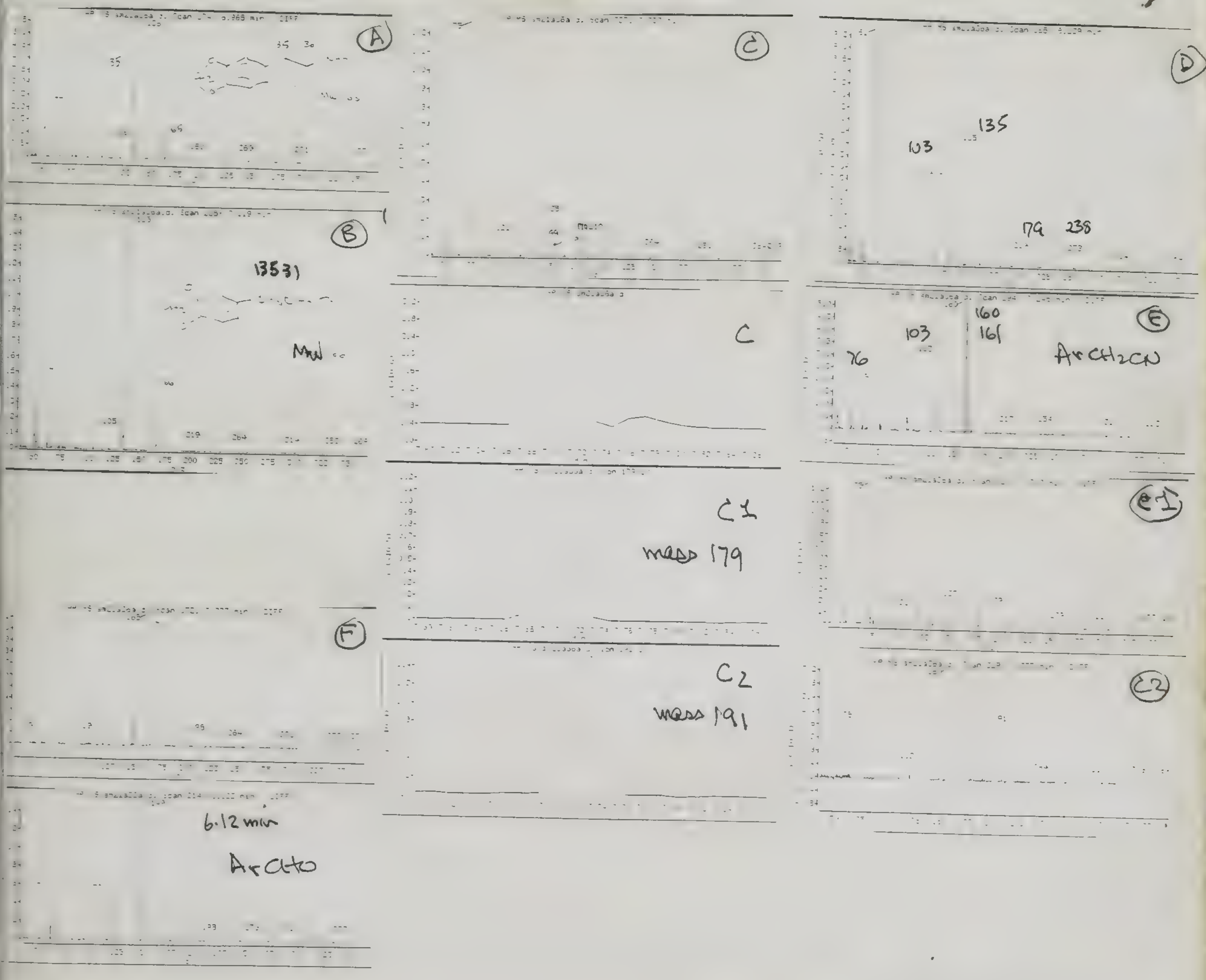




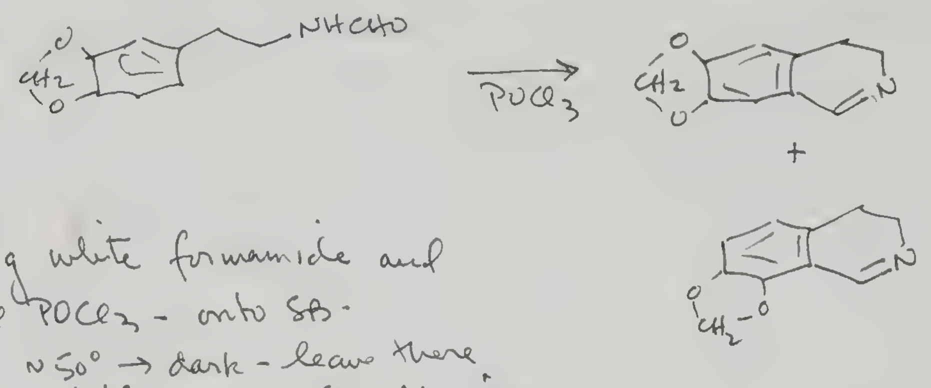
neutrals from  NO2 $\xrightarrow{Al(Hg)}$

See page 208





194



2.30 g white formamide and
10 ml $POCl_3$ - onto SB.
Δ - ~50° → dark - leave there
a while 11PM off mid night.
to RT ON - (cold room!). into 150 ml H_2O (also cold) c̄
good stirring - goes to ~35° - orange brown aq. c̄ a
film, an oil of insolubles. Aq. quite acidic, distribute
between H_2O & 60 ml CH_2Cl_2 Red in aq - yellow in dichlor. *
All aq to pH >11 c̄ 25% NaOH * all sets up solid!!! * It takes
~600 ml H_2O to get stuff loose - and almost into solution -
xtrt c̄ CH_2Cl_2 3×75 mL -
even now aq not a totally
clear soln!

(when poured in sep funnel)
bubbling! once basic - no more

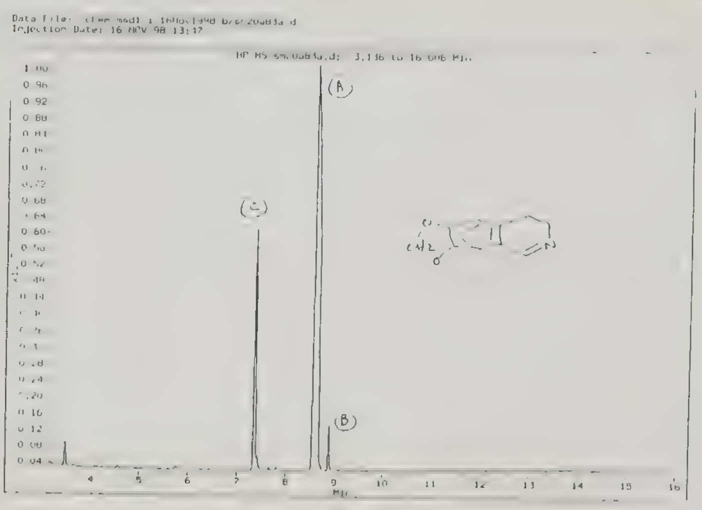
flash.

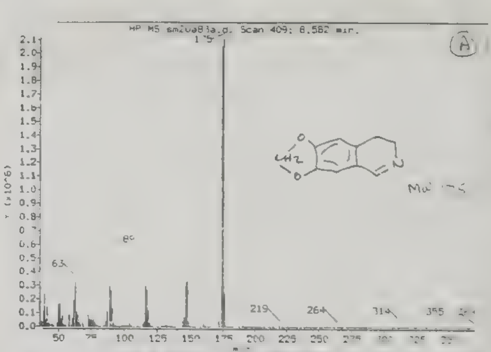
neutral fraction -
flash 0.46 g viscous
brown oil 194-A
to GCMS
SM20 A86A
starting amide, DHIQ 2:1

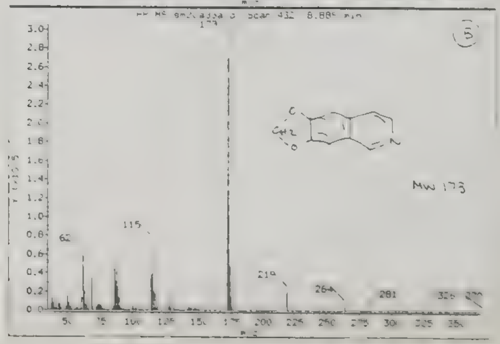
→ 1.59 g amber oil
to KR - starting to xtallize
120-130° @ [illegible] 40μ. white oil that
immediately goes to white xtals!
considerable black oil left in pot. won't push it
Off - white solid - receiver 1.25 g (194)

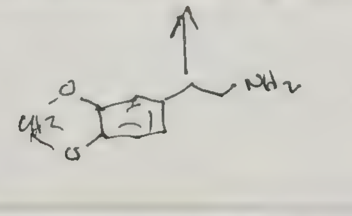
SM20 A83A

20μ
100-102 μ.
110° white liquid



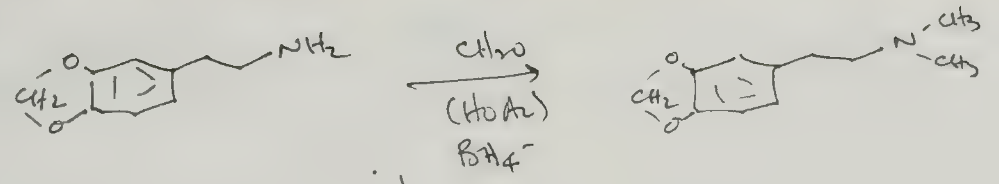






≡ page 190 reference

from page 187.



0.40g base - now known - into
{2 ml HOAc / 8 ml MeOH} to RB c̄ mag stirrer add
2 ml 37% CH2O -
1.5g NaBH4 - spatula - wise - over 20 min. - foaming over - added squirt of HOAc - no more foam - stir.

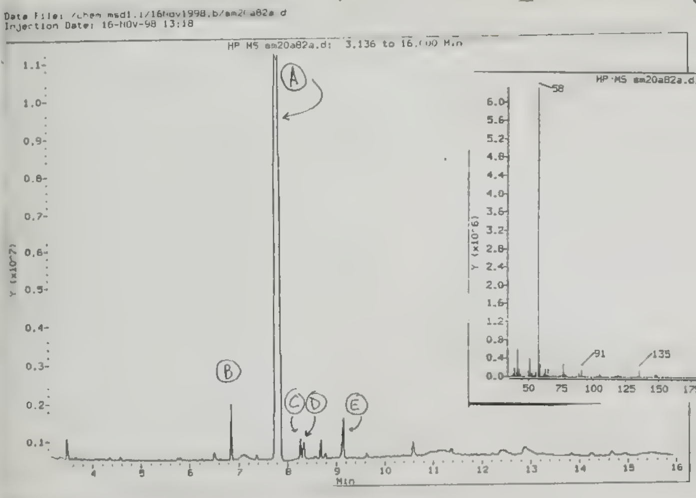
stir ON R.T. - into ~100 ml H2O - + HCl → strong H+ -
wash 2 x 50 ml CH2Cl2 → neuts. OUT

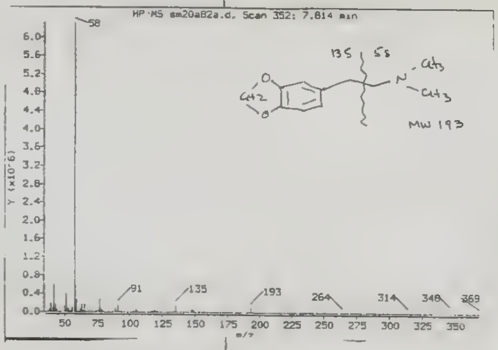
+ 25% NaOH
xtract c̄ CH2Cl2

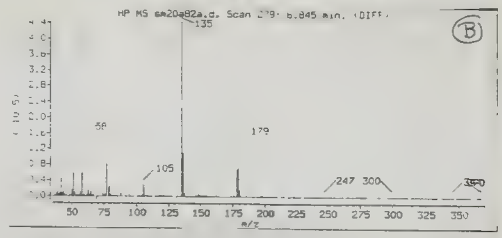
emulsion
spin both times.
0.25 g pale amber oil
KR 0.02μ. 95-105° ~ (0.22g) not quite white oil - no - it's white!

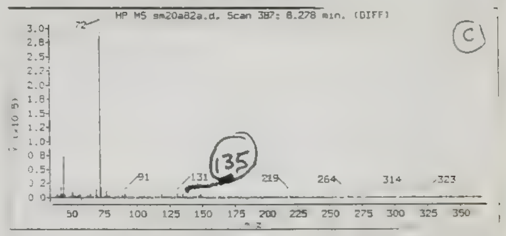
→ into 1ml IPA + conc HCl
2 not enough 4 drops too much
start xtals + 2 ml ether - drain
p plate .175mg white xtals.
2nd crop + 15 mg combine

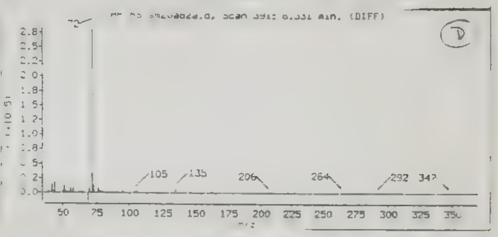
GCMS (195)
SM 20 A82A

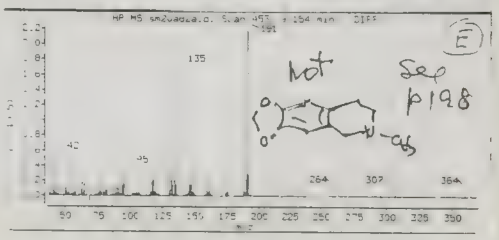


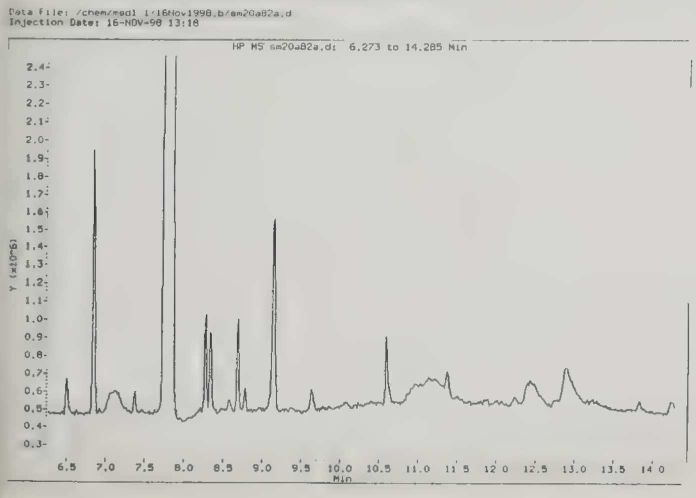




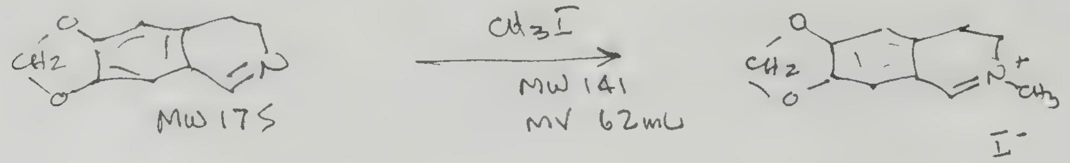








(196)



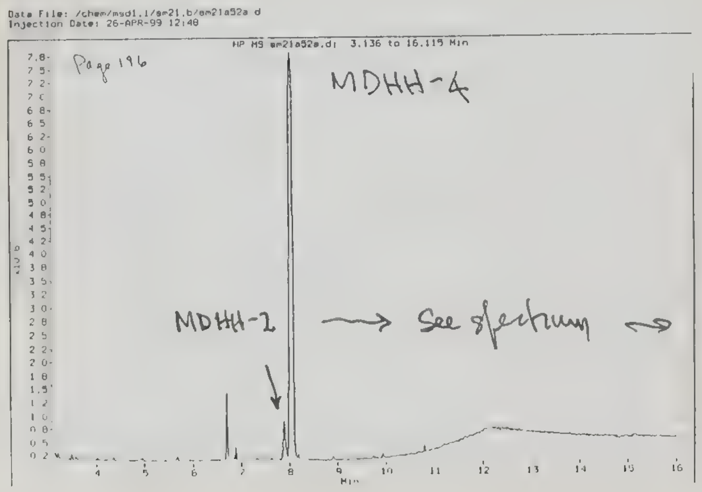
0.6 g DHIQ (194) into
1.0 ml MeOH - Δ → sol ∇ still solution, +
0.3 ml CH_3I (~50% xs), immediate yellow color - Δ on Rot. Evap -
∇ - nothing - Δ again ∇ RT → fine xtals - develops more
and more - all soon solid - add ~3-4 ml MeOH - solids disperse
but not all dissolve. Stand. RT a few hours - yellow solids.
filter - wash cautiously c̄ MeOH -
wet weight (yellow xtals) 0.55 g.
0.42 g dry
0.38 g on to reduction

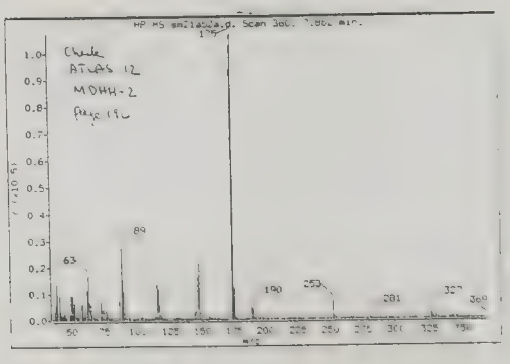
Save 0.04 g ref. (196)

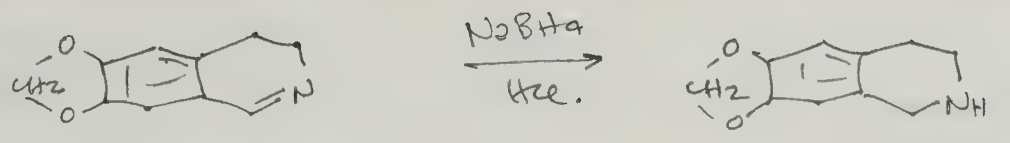
ML'S → yellow xtals - onto plate. 196A
116 mg
recryst a bit from MeOH
(IPA too insol)

(Repeat - on page 222)

Work-up of 0.49 g (197A) - now turned slightly off white. dissolve in 3 ml hot IPA (1½ not enough) add 12/14 drops conc HCl → solids, off white, filter without ether - wash c̄ small amt IPA - then final c̄ small amt ether → 0.43 g off-white MDHH-4. HCl (197B). :M21A52A







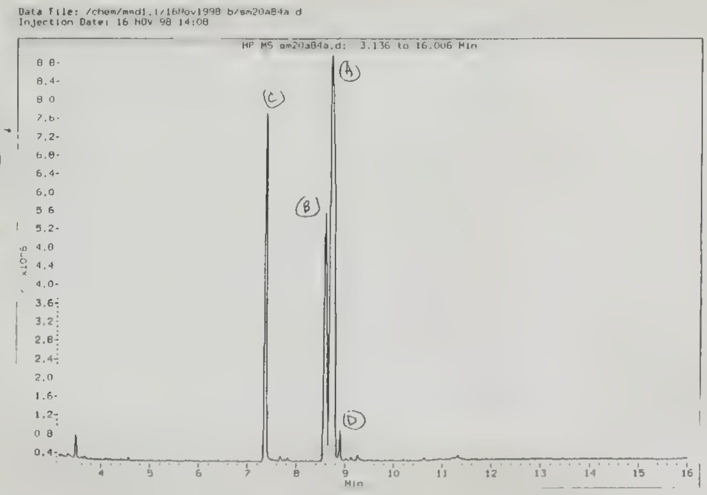
MDHH-4

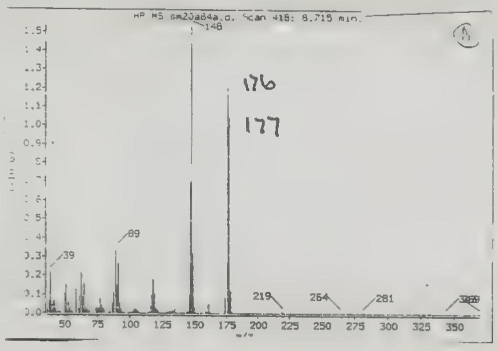
0.6 g DHIQ 194 into
~10 ml H_2O – HCl dropwise → yellow solution (~10 drops) add
0.6g $NaBH_4$. immediate yellow loss – foam – then towards end – more of a froth. add
20 ml H_2O – not much change – add
several cc 1 N HCl .. some foaming – solution largely clears, and no more response to HCl.

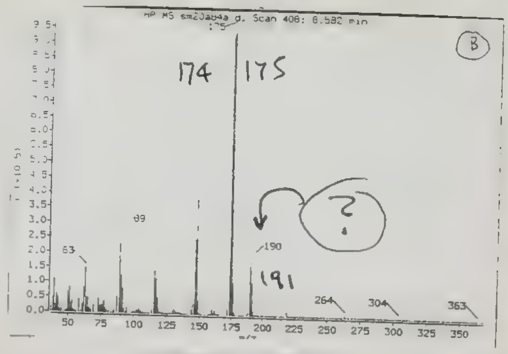
strongly acid – xtrt 2 × 40 ml CH_2Cl_2 ⟶ neuts
OH^- c̄ 5% NaOH (get new pH paper!) – xtrt
3 × 40 ml CH_2Cl_2 – flash → 0.56 g white crystalline solid. to KR. (*)
over 90°–100° 60 m. → (0.4g) fused white xtals
into scint. vial. (197) small sample for GCMS (197A)
SM20 AB4A

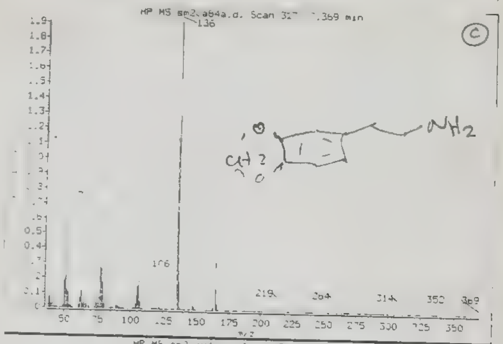
(*) 50 m 50° –
60 m 90° oven

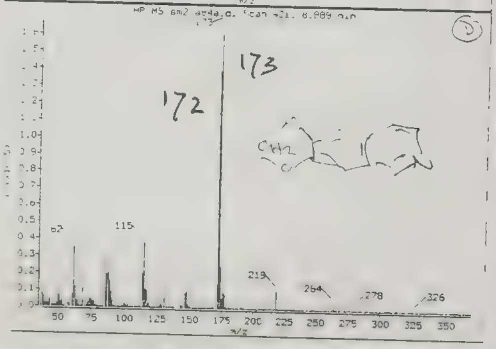
Data file: /chem/mnd1.i/16Nov1998 b/sm20ab4a.d
Injection Date: 16 NOV 98 14:08



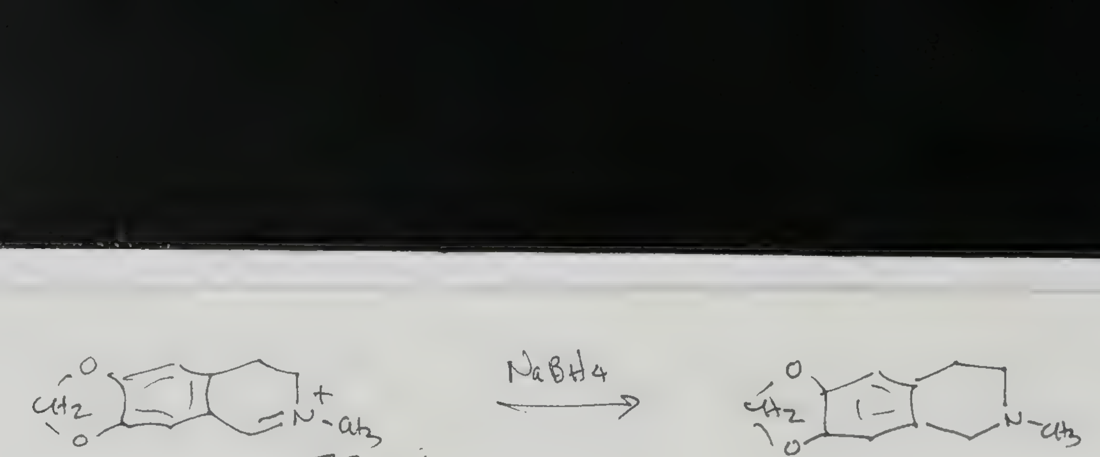








(198)



MDHM-4

0,38 g yellow xtals, 10 ml H_2O – not completely soluble – add some 1N HCl – no better – add

0.38 g $NaBH_4$ (some eth. add more HCl – finally quiet – color however completely goes. + H_2O + HCl – xtrt 2 x 50 ml CH_2Cl_2 ↳ neuts.

OH ī 5%, then 25% base → white cloudy – xtrt 3 x 40 ml CH_2Cl_2

0.16 g base on R.E.

0.16 crude base

85-95°/50 μ. over white oil ! pot ī liq.

push T. to 130° – still pot oil. nothing more. stop.

K.R. → white oil 85-95°/50 μ. considerable pot residue

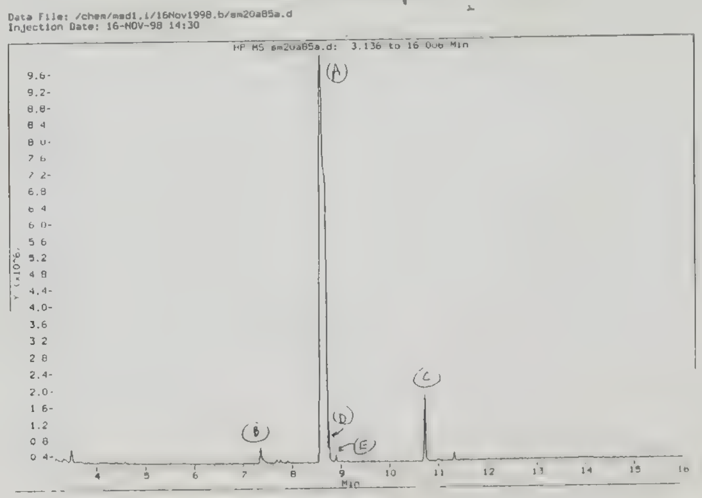
100 mg white oil.

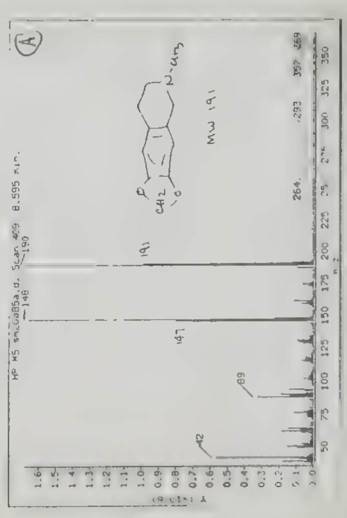
small sample ī dry ice → xtal – tubes.

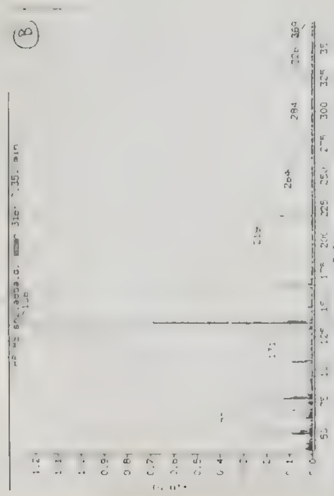
Scrape out 0.08 g 198

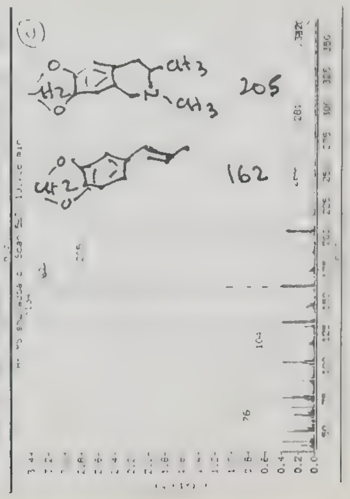
small sample GCMS

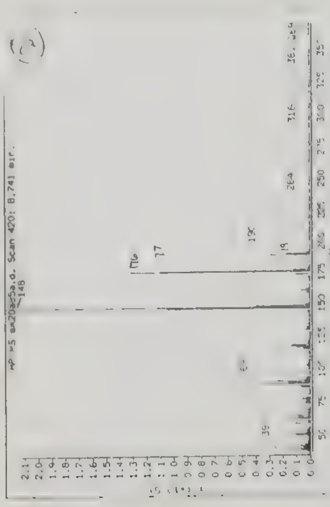
SM20A85A

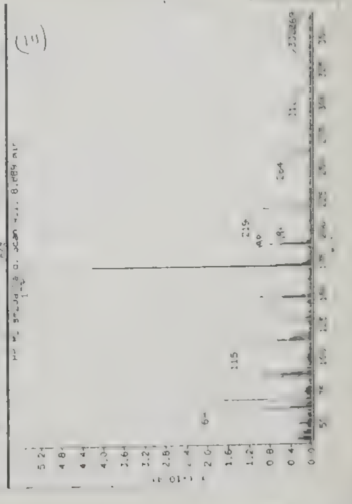




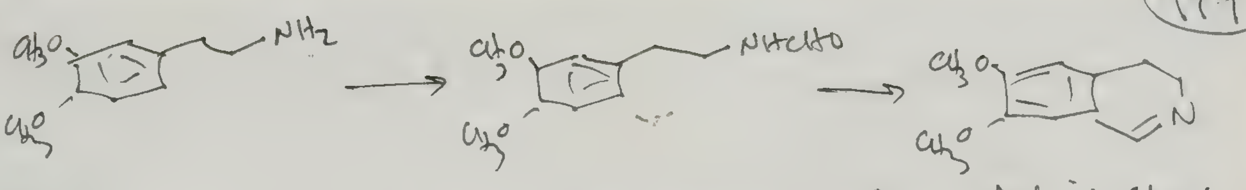








Repeat.



See 170
171

10 g DMPEA, saturated c̄ carbonate - the ancient bottle of Aldrich chav. stuff - all that would drain - carbonate now solid in bottle.

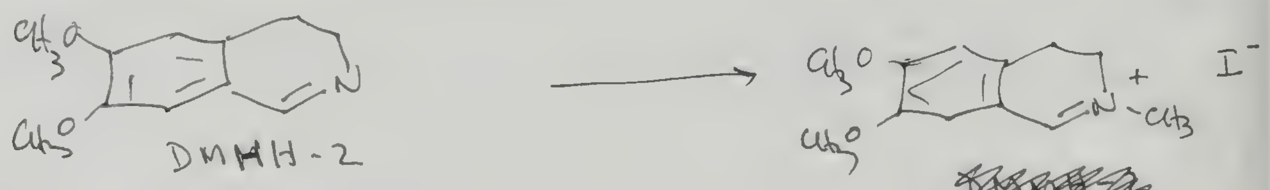
25 g isobutyl formate → cloudy - Δ SB 1 hr ⇒ brown soln. - add to 200 ml H_2O, @ → pH ≤ 1. extract 3 × 75 ml CH_2Cl_2 - pool - wash c̄ 5% NaOH - flash → ~~[illegible]~~ 10.85 g ~~viscous~~ oil - ~~visc~~ distil crude

KR 130-160°/120 μ, → 7.52 g viscous oil pale amber. into 45 mL $POCl_3$ - spill - nasty - onto SB 1 hr (1.5 hrs actually.) - off - cool ON. Into 400 ml cold water - exotherm of course - ∇ c̄ H_2O - xtrt c̄ 2 × 50 ml CH_2Cl_2 → neutrals
OH^- c̄ 25% NaOH to pH ~13 - ∇ → solids, H_2O to 1300 mL to dissolve. xtrt in ½ batches c̄ 3 × 50 ml CH_2Cl_2 each - pool. wash c̄ H_2O - flash → 4.24 g viscous brown oil. KR.

200 μ 130-140° 2.73 g. save ~0.2 g to see how the oil discolors colors.
2.50 g to page 200

neutrals ↔
→ this all from memory - lost the paper c̄ the notes and weights. flash of CH_2Cl_2 → a lot of material - 2-3 g

2.16 that tends to go solid. TLC a bit checking against reference sample of formamide.. solvent 80/20 hexane/EtOAc. Amide ~0.2 Rf. this stuff origin. Could the salt of DMHH-2 be extractable into CH_2Cl_2 !? Partition ~~against~~ in OH^- H_2O & CH_2Cl_2 - CH_2Cl_2 to dryness ~1.5 g? to KR. So, so vacuum (~200 μ?) and push to ~200°. Some 60 mg came over and the pot was left with a dark residue - too much - with some fluidity. OUT.



DMHH-2 → DMHM-2

(ex page 199)

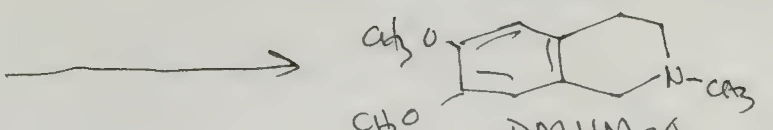
2.50 g DMHH-2 - dissolved in
5 ml MeOH - add
1.2 ml CH_3I.

Δ on edge of SB - - suddenly yellow xtals - off - let stand to RT - development of orange xtals pushing up through the yellow! Stir it all uniform - let stand. washing the stirring rod does not remove the quat.

Filter (after adding a couple of ml of acetone. → gold colored xtals - wash 2 x 2 ml acetone - suck dry - air dry.

↳ 4.29 g (not dry)

4.20 g dry



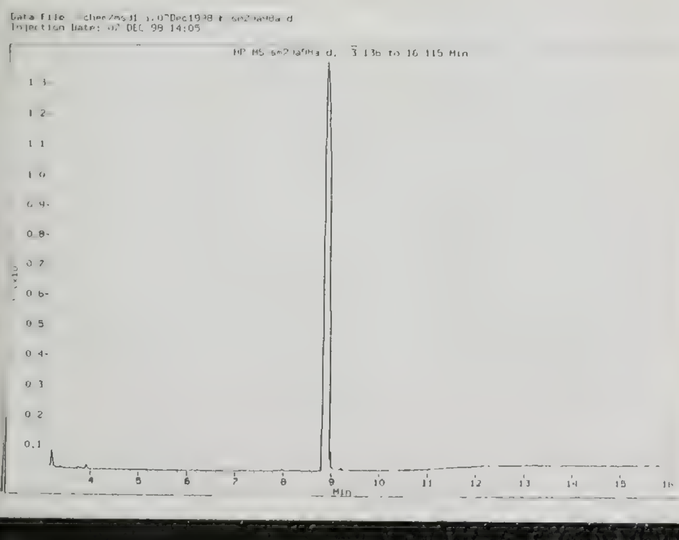
DMHM-4 MW 207

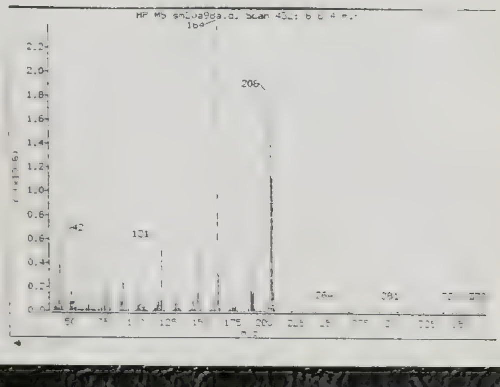
4.0g gold-orange xtals f. p200, into 100 ml H_2O squirt of N HCl - not quite clear, but very yellow, solution
1 g $NaBH_4$ added a bit at a time, with occasional squirts of N HCl. Color dissipated with the first bit of BH_4^- add 5%, then 25% NaOH to pH > 10 - heavy gel of maybe sodium borate? Dilute to ~ 600 ml c H_2O which pretty much clears it
xht c 3 x 50 ml CH_2Cl_2 - absolutee colorless! pool, flash
→ 2.46g crude white oil, xtals in flask - KR →
!! 2.76g white oil that distils at 120-130°C at 300 μ
reweigh when dry out of the receiver. Beautiful GCMS.
SM-20-A98A

picked out the rest
1.94g → 1.84g to HCl
dissolve in 9 mL IPA.
Δ needed. ∇.
+ conc HCl (theo ~ 15 drops - used ~25 - small drops? start of xtals
+ ~ 6 ml ether →
heavy white mass - filter wash w ether + IPA, then ether
white air-stable solids,
recrystal CH_3CN - fair →
recrystal EtOAc - bad
recrystal MeOH, too sol.
recrystal IPA. fine →
crude wp →

← 0.10g 201 certainty GCMS - if same as this, combine & hold as reference

0.1g white xtal - I am pretty sure I started pick it out when the big Sunday occurred
to GCMS as probably ←





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THE CONTROLLED SUBSTANCES ACT

A RESOURCE MANUAL OF THE CURRENT STATUS OF THE FEDERAL DRUG LAWS

Including:

A 215 page chapter that lists every formerly and currently scheduled drug, the authority for its inclusion in the law, its exact chemical name, its Chemical Abstracts identification number, and all known synonyms for it.

A history of the development of the currently employed Federal law, and the many amendments, changes and regulations that have brought it into its present form.

A complete listing of all chemical structures of the controlled substances, arranged by structural families.

Some 46 pages of Drug Code Numbers assigned to drugs, solvents, vitamins, food stuffs, and even things unrecognized.

All Federal Register Citations that have been used to justify changes in law and regulation.

A complete empirical formula index of all compounds mentioned in the current statutes.

Four appendices, detailing the original law (1970) and the present form it has taken (1987), the wording of the Emergency Scheduling Act, the Analogue Enforcement Act, and the currently available and

35.519

35.566

tare → 33.800 1.766

35.519 1.719 worst↑

35.466 1.666

35.455 1.655

---

page 198

0.38 g 10 ml H_2O not comp sol

+ N HCl

0.38 g $NaBH_4$ color never completely goes away

page 219

1.09 quat (MDMM-2) 40 ml H_2O

+ then 3.5 mL N HCl

add .4 g in bits + squirts N HCl

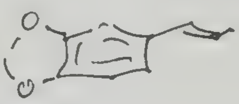
---

here 1.65

50 mL H_2O

.6 g BH_4^- ~5 mL N HCl

(202)

accumulate 

25 g piperonal
75 ml CH_3NO_2
2 1/2 g NH_4OAc
Δ SB 2+ hrs. – into beaker – ∇ cold hrs
~4 hrs filter – wash c̄ a little MeOH
air dry.

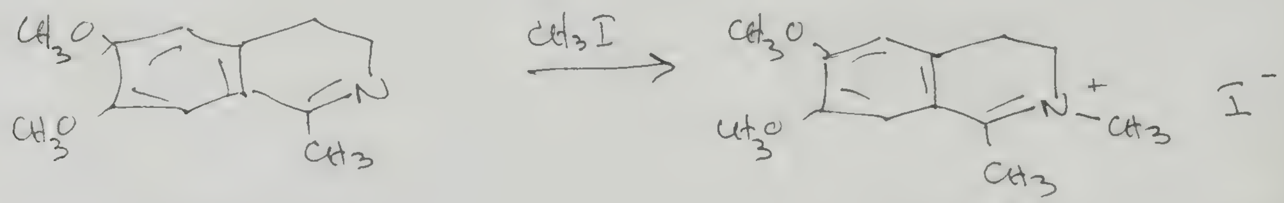
189B
5.73 g crude –
check MP! OK!
Δ SB c̄ 75 ml ~~[illegible]~~ AcOH
Δ SB 1/2 hr.
filter hot – removing
some insol's.
∇ O/N RT

3.34 g

Inquiring into the "Pharmayasca" available in Palenque

5-MeoDMT pill | [H] pill.

5-MeoDMT pill	H? pill. dirty yellow
	235 mg
	Lost the quan-
	sprayer
	[illegible]
	whats left?
	30 mg white solid
	H₂ harmaline · HCl
	Sigma Lot 123H3717
	95%
	H₀ Harmine · HCl
	~~B~~ H0002 Lot AJ01



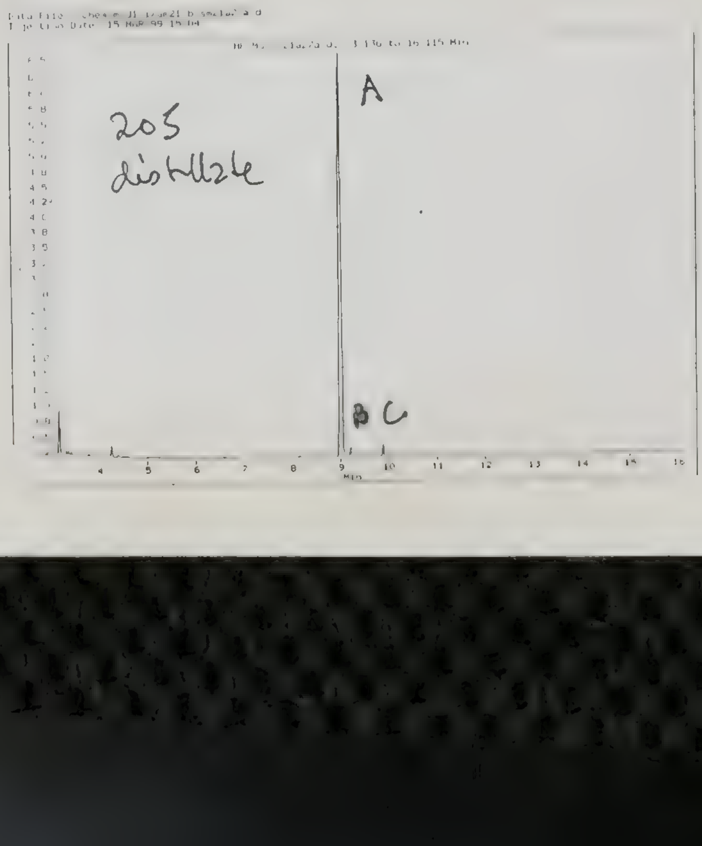
DMMH-2

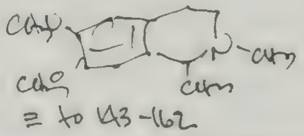
DMMH-2⁺ I⁻ MW 347

2.70 g DMMH-2 base 169-C - dissolved in
5 mL MeOH - all goes in - off white solution - add
1.2 mL CH_3I - Δ on Edge of SB 15 min → yellow color -
not too deep - friendly - off - and while quite
warm scratch with glass rod - eventually → soli - all
takes ∇ RT - pale cream xtals - sets up pretty
solid. - add 3 mL acetone - filter - wash sparingly ē acetone
↳ 3.56 g extremely pale yellow xtals air

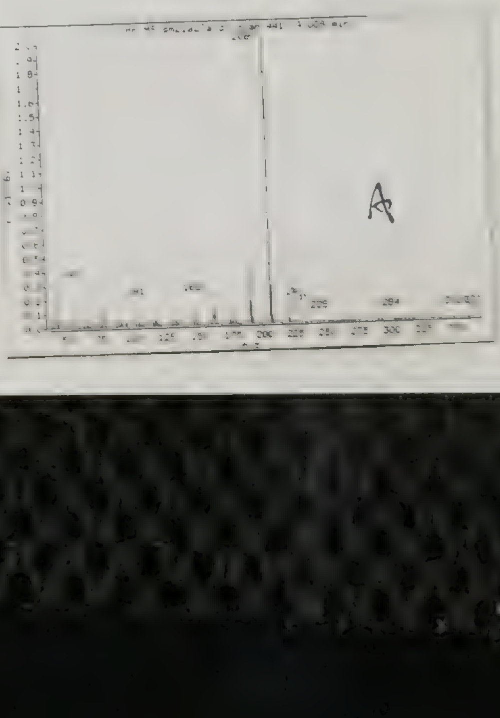
(204 A) save 100 mg for mp, etc.

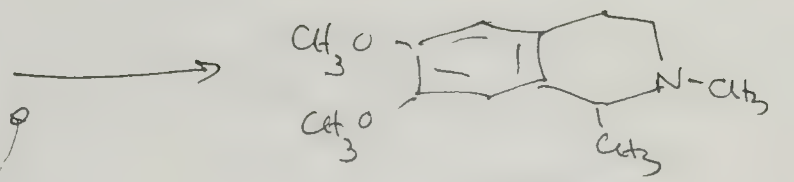
it looks like it has some acetone solubility - ML's + acetone washes →
more xtals - 60 mg
+ 200 mg 204A } 260 mg recrystallize from 0.6 mL MeOH
0.6 mL MeOH.
in hot - clear pale yellow soln.
∇ ē cold water → ~ white xtals
200 → 194 mg white xtals
save for mp, NMR
(204 B)





≡ to 143-162





DMMM-4

~~KHO 3E7~~

Carnegine
Merck index
#1896
viscous oil
HCl·H2O ex dil EtOH
mp 207
anh. 221

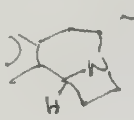
3.36 g NMe quat DMMM-2$^+$ I$^-$ into 100 mL H_2O - add just > 10 ml N HCl (~~[illegible]~~ molar quantity) and add 1 g $NaBH_4$ a bit at a time.

quat in water cloudy. add ~12 ml HCl - still cloudy & no color at all! pH red. add 100 mg globs of $NaBH_4$ - no exotherm ~ 1/3 of BH_4^- added now green, squirt x4 N HCl → red - alternate 100 mg BH_4^- + squirt HCl always letting the pH dictate which next. 1/2 way through - totally clear aq - soln - & no trace of color - add rest of $NaBH_4$ + acid to leave the pH red. - xtrt 2 × 50 ml CH_2Cl_2 (let evaporate) OH to blue ē 5% NaOH. xtrt 2 × 75 ml CH_2Cl_2 - no emulsion - clean - pool - flash → 1.56 g pale yellow oil,

KR. 115-125°/50 μ

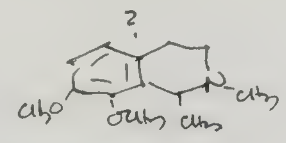
50 μ.
100° no
115° barely going
125° done
white distillate
clean pot.

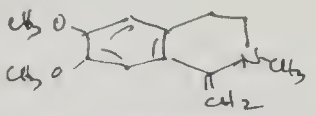
1.56 g (205A) save small sample GCMS. see page 204
rest into beaker ē 8 ml IPA. + conc HCl 21 drops not enough, 24, more than enough - then - white xtals start to form - in 2 min very thick - dilute ē 5 ml ~~ether~~ - filter - wash ē ~~ether~~ acetone (sparingly) acetone → 1.94 dry wt IR

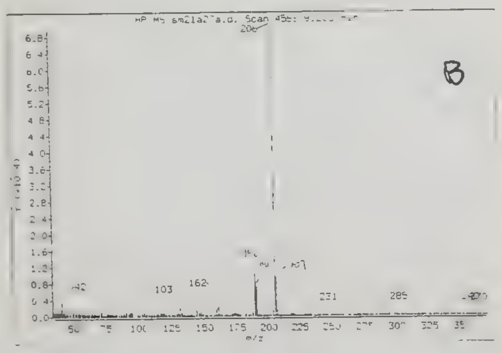


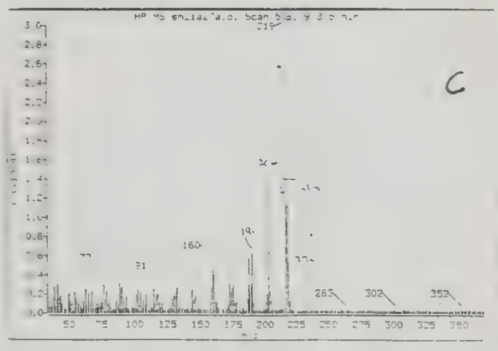
? 1.78 really dry.
(NOVA) ☆
or some-such
MW 219

1.94 dry HCl









DMMM-4
minus
2
Hydrogens

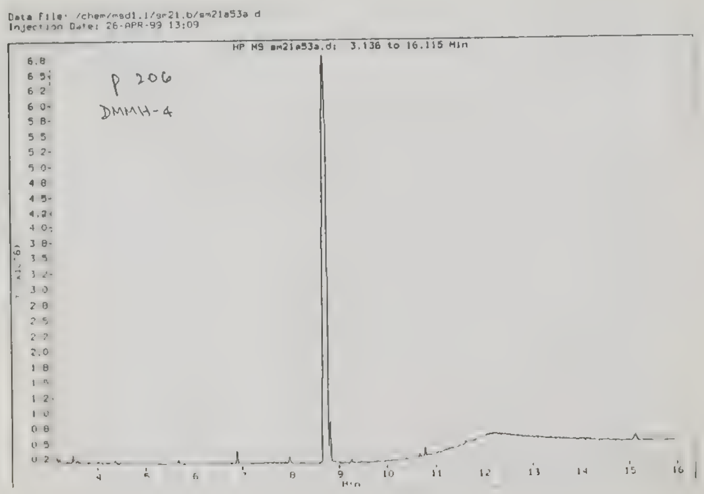
(206)

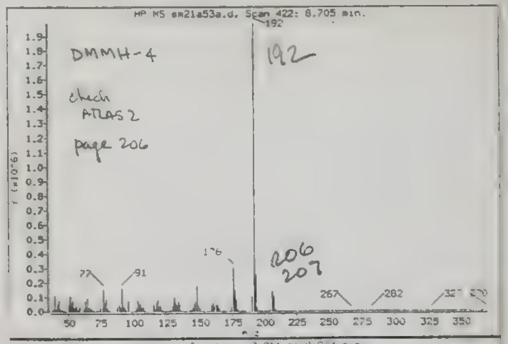
DMMH-2 → DMMH-4

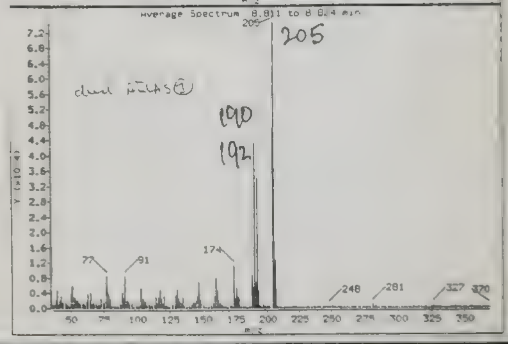
1205 2.6 g DMMH-2 (page 169 C) MW ~~221~~ ~~207~~ 205 ~ 12 mM into
100 ml H_2O (IT IS WATER SOLUBLE !!!), acidify with
1 N HCl (~ 12 ml or more → red pH paper)
1 g $NaBH_4$. add a bit at a time (good stirring) + N HCl
as needed to keep the solution acidic. No exotherm.
wash c̄ 50 ml CH_2Cl_2, basic c̄ 5% NaOH – extract 2x
50 ml CH_2Cl_2 – strip on R.E. → "1.17 g" crude – obviously
I misread the balance, see below – KR 110-120°/40 μg →
2.13 g free base – white oil – ON start of xtallize

picking up CO_2? GCMS conc A31A (SM21)
save a bit of free base solids – contains CO_2 dilute A33A (206A)

Partition between CH_2Cl_2
and dil NaOH – 3 xlts –
flash → 2.24 white oil – dissolve in 8 ml IPA – 30-32 drops HCl →
pH red. no xtals – add ether to turbid – no xtals – forget it out
externally – seed – sorta takes – I feel I am fighting two xtals?
(hydrate) – more ether → mush of solids – filter – wash c̄ ether –
air dry → 2.70 g spectacular white solids – ether slow to evap. ·1.0 H_2O?
(206B) acetone soluble!! but the carbonate is not!







DMHH-2 → DMHH-4

1.5 g DMHH-2 ·HCl (from p172A) - into 50 ml H_2O

0.5 g $NaBH_4$ - + 1N HCl

With good stirring add hydride a bit at a time, keeping the Rx mix acidic c̄ squirts of N HCl. Wash c̄ 1×30 ml CH_2Cl_2, ~~extract c̄ 2×40 ml CH_2Cl_2.~~ make basic c̄ 5% NaOH, extract c̄ 2×40 ml CH_2Cl_2 - flash on R. evap → residue that crystallizes. Distill at KR 110-130° 100 µ - all sublimes over as white solids. Wt (in flask) 1.12 g

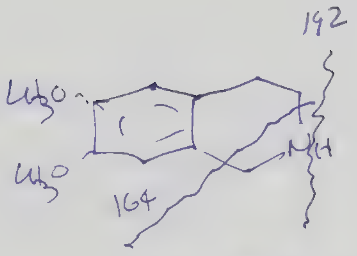
scrape out. 1.00 scrapped out - not sol. IPA, sol. H_2O - it must be the carbonate - into ~100 ml H_2O some soluble - add 5% base → pH blue - xtrt 3×40 ml CH_2Cl_2 - flash →

~~[illegible]~~ .86 g oil that sets to white xtal - dissolve in 2 ml hot IPA - into beaker - rinse c̄ 2 ml IPA - clear soln - add 10 too little 13 too much HCl (solids at 3!) + a bit of ether - stand - filter - wash c̄ ether air dry → beautiful white crystals of DMHH-4 ·HCl 0.92 (207A)

C. Reading
6, ~~7~~ MeO MeO

6,7 MDO

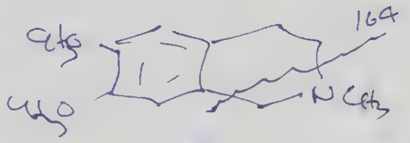
H,H 207A p178
MW ~~[illegible]~~ 193



193 ~~[illegible]~~ 60%
192 ~~[illegible]~~ 55%
164 100%

1,7B
MW ~~[illegible]~~
177

~~[illegible]~~
H,Me 201
MW ~~[illegible]~~
207



~~[illegible]~~ 207 ~~[illegible]~~ 50%
~~[illegible]~~ 206 75%
~~[illegible]~~ 164 100%

223
MW ~~[illegible]~~
191

~~[illegible]~~
Me H 206B
MW ~~[illegible]~~
207

?

218A
MW ~~[illegible]~~
[illegible]

Me Me 200
MW ~~[illegible]~~
221

219
MW ~~[illegible]~~
205

(208)

8.2 g Al 1" squares (~2 ft foil) - add solution of .22 g $HgCl_2$ in 300 ml. H_2O, at RT ~1/2 hr → heavy grey, bright
Stops - H_2↑. - decant H_2O, wash
300 ml H_2O - drain, ~~add~~ wash
160 ml IPA - drain - add
+ [160 ml IPA, 16 ml conc HCl] - add - over 1 minute ;
3.34 g (see page 202) NS. in 40 ml MeOH
40 ml IPA Δ SB - not in solution -

extremely exothermic - ∇ ext. H_2O. 20 min done. almost no Al left.
add conc HCl until red c̄ pH paper. Try extracting c̄ CH_2Cl_2
(dichlor top phase!!) separate c̄ pasteur pipet - GCMS on
these neutrals see page 193 dilute c̄ about equal volume H_2O.
lots better - dichlor on bottom - extract again → orange red neutr.

aq. basic c̄ 25% NaOH - xtrt 3 x ~75 ml CH_2Cl_2 (done in three batches - dichlor amts are approximates - pool - flash on rot. evap. → 1.8 g brown oil

distill at 40 μ 90-100° white oil 0.95 g (208C) → all - next page
pot, lots, ~~not~~ even up to 140°. - flick for GCMS (208B) → OUT

90° 0.04 over white oil

flash ?
2.32 g
Save most under the amine
see p 193
(208A)

Snorkel → white solids.
Carbonate (save)

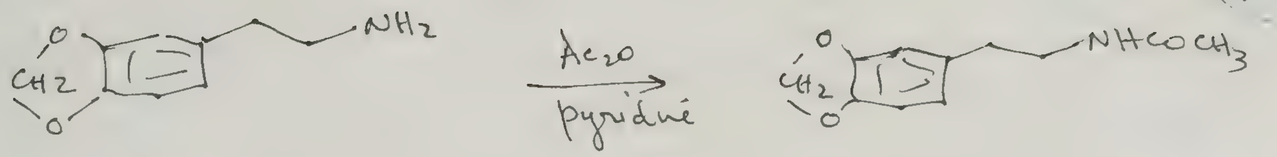
wendy preps 1, 2 & 3

run # 1 1.54 white oil used for acetamide 215

#2 crude 1.46 g
#3 crude 1.87 g
3.33 g

Kiz 95-105° 50 μ pot residue push to 135° still pot residue STOP
→ white oil 2.542 g all to formamide page 220
& 0.712 pot residue non-vol. at 140° C. carbonate? (208D)

See page 261

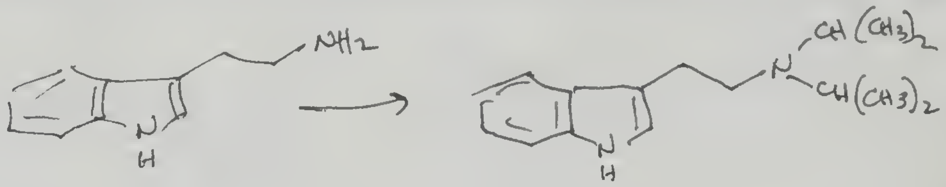


0.95 g white (208C) into 2.5 mL pyridine - add
1.0 g Ac_2O. Δ S.B. 1 hr. (tried to strip it. no go). add to
30 mL H_2O - add globble of NH_4OH - stir - oil goes to
solids. color pale tan, but that may be some of Jill's
junk out of the snorkel of the rotary evaporator - took
for that awful p-bromoanisole
filter - wash c̄ H_2O - kinda dry → 0.92 g off-white solids
aq. H_2O c̄ 5% xht c̄ CH_2Cl_2 - wash acid (1N HCl) flash
→ 0.19 g

distil at KB 165–180° at 0.08 μ. white oil over.
0.150 μ. Say 165–185°! spont. xtals.
0.83 white crystals (209)

(210) Repeat -

try



1.60 g tryptamine

10 g N-methylpyrrolidone soluble

6.5 g diisopropylethylamine 2 phases

8.5 g iPrI - one phase again (unlike c sulfolane)

onto steambath 4 PM. ~8 PM darkened - 2 phases? → sets to xtals H_2O sol. some HI salt

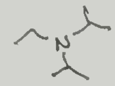
off 11 AM = 19 hrs. very dark - 2 phases? * Add H_2O to the 200 ml work -

~~[crossed out]~~ is strongly basic - xtrt c 3 × 50 ml CH_2Cl_2 - all color into org.

xtrt c Dil. HCl 3 × 50 mL (color stays in CH_2Cl_2) - pool aq.

wash 1x c 50 ml CH_2Cl_2, make aq. basic (blue) c 25% NaOH.

cloudy - xtrt 3 × 50 CH_2Cl_2 - amber colored - flash. at 80°/0.05 μ -

all the  is gone → black heavy oil in pot. Δ at 90° - I

notice some colorless oil in the receiver - was it there at

80°? - yes probably - lots up the snorkle - no smell - must be

N-MeP-one 1.2 g and more. New receiver.

(210A) GCMS

.05 μm

110° bonding?

140-150° over ≐ 0.76 g pale amber (210B) - pot black! pot out with 4 ml IPA

dissolves slowly - OK + 7 too little 10 too much drops of

conc HCl. Spont. xtals + a little Et_2O. nice white

xtals - wash c ether/acetone. air dry → 0.52 g xtals.

21% yield! ugh

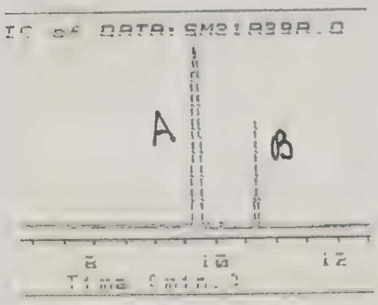
(210C)

ML's 2nd crop

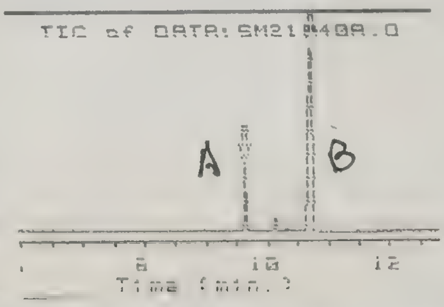
0.13 g white xtals (210D)

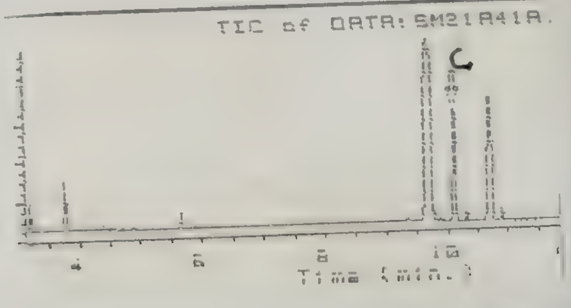
(210B) #41

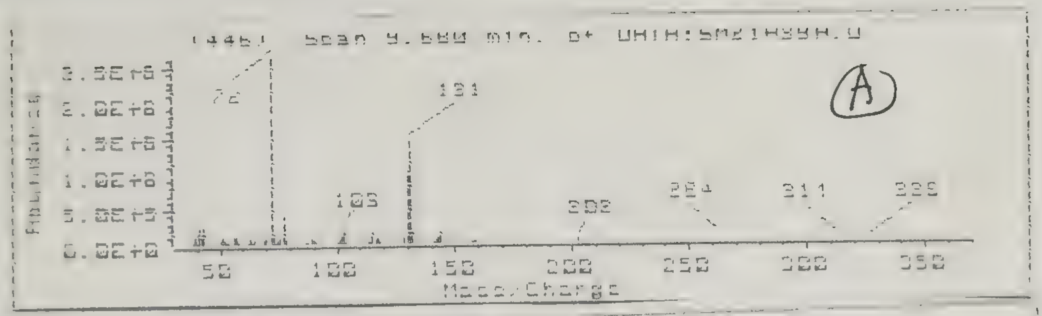
(210C) #39



(210D) #40



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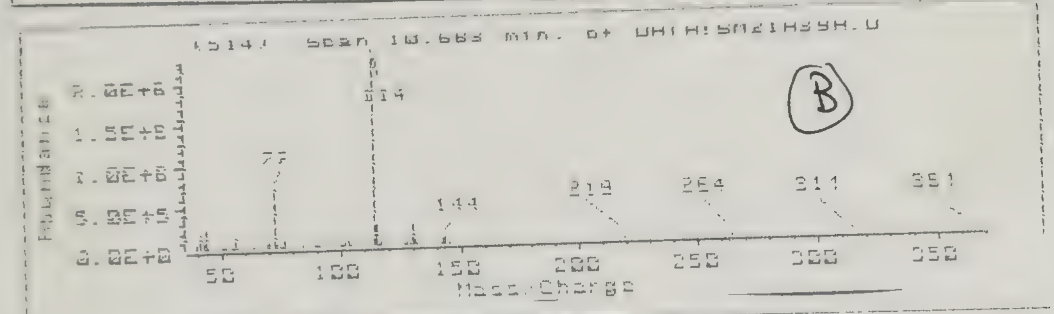
Abundance
Mass/Charge
A
72
131
105
202
264
311
335

NIPT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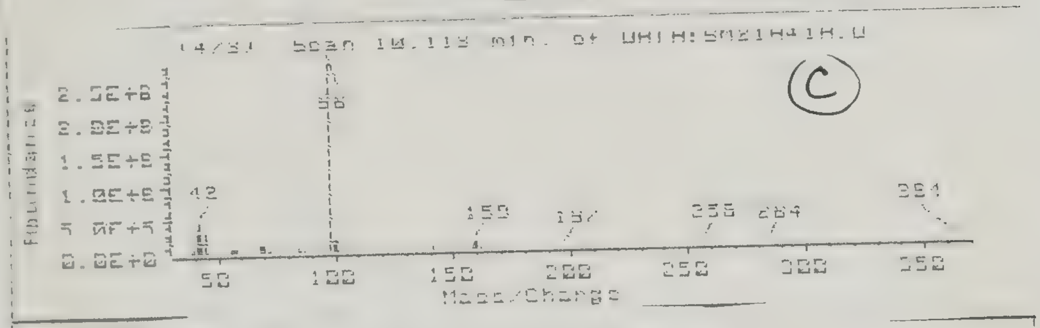
Abundance
Mass/Charge
B
114
77
144
219
264
311
351

DIPT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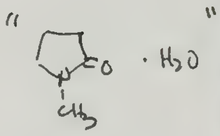
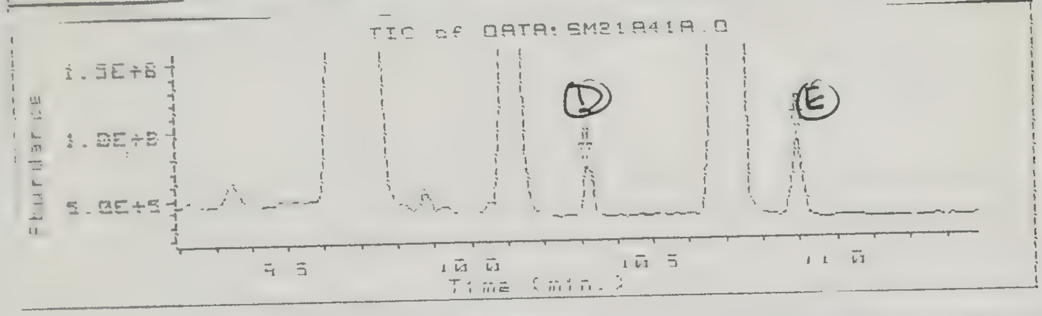
Abundance
Mass/Charge
C
98
42
159
187
255
284
351


" · H_2O "
CH_3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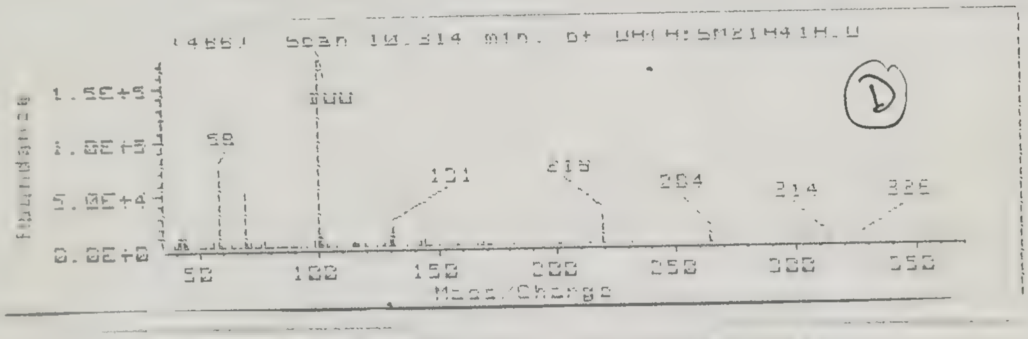
Abundance
Time (min.)
D
E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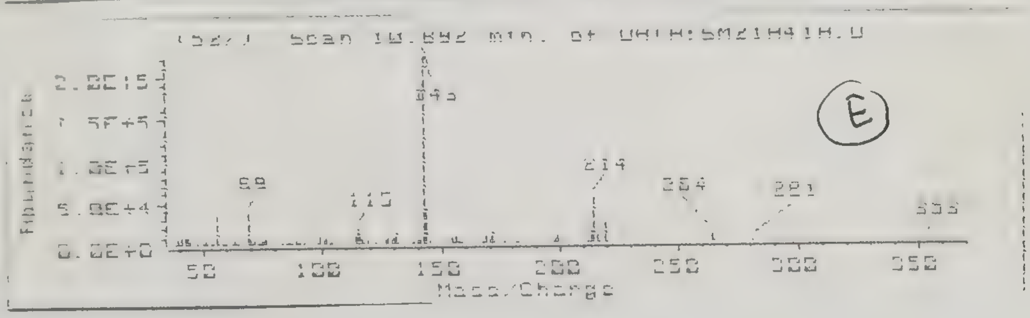
Abundance
Mass/Charge
D
100
58
131
218
264
314
326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Abundance
Mass/Charge
E
145
69
115
214
254
281
335

SAMPLE TABLE SM-21 Rev. 1.1 1-May-89

Sample table file name: [redacted] 22 Mar 99 4:56 pm

Index	Sample identification
1	DMMH 4 PAGE 206
2	DMAH-4 PAGE 207
3	#31 DILUTED 20%
4	#31 DILUTED 20%
5	BUPROPION METABOLITE "MORPHOLITE" 1000UG/ML
6	BUPROPION ERYTHRO-ALCOHOL METABOLITE 1000UG/ML
7	COTININE 1000UG/ML
8	SHIFF'S BASE/CERIUM REAGENT
9	#201 DMMH 4 WITH CERTAINTY
10	#201 DMAH-4 WITH HIGH PROBABILITY
11	CHCL3 EXTRACT OF BICARBONATE AQUEOUS OF WHITE SEED POD
12	REPEAT OF 11
13	TS RXN
14	SEC ALC
15	SUSPECT 5-MEO-DMT
16	SUSPECT HARMALINE
17	PHENYL-PYRROLINE?
18	N-MS-MVD ANALOG, FISHER
19	REFERENCE HARMINE
20	REFERENCE HARMALINE
21	SUSPECT HARMALINE AGAIN (SEE 16)
22	75% EXTRACT, IN 90/10
23	50% EXTRACT, IN 90/10
24	25% EXTRACT, IN 90/10
25	STEM EXTRACT
26	TOP EXTRACT
27	PAGE 205 DMAH-4 NEW SYNTHESIS (FROM DOAH)
28	PAGE 143 DMMH 4 OLD SYNTHESIS (FROM DMMH WITH CH2O)
29	"B" OF SKULL-CAP 3/15/99
30	"E" OF SKULL-CAP 3/15/99
31	DMMH 4 PAGE 206
32	DMAH-4 PAGE 207
33	#31 DILUTED 10%
34	#31 DILUTED 10%

95
96
98
99

95 page 423 T.l.
96 page 39 as is T.l. "D"

98 page 39 (base) D T.l.
99 page 41 (base?) F T.l. book

S A M P L E   T A B L E   SM-20   Rev. 3.2 11-May-88

Sample table file name: [redacted]   2 Nov 98   5:40 pm

Index Sample Identification
1 MENTHO D0
2 MENTHOL-D4
3 MENTHONE-D0
4 MENTHONE-D2
5 PHENYLACETALDEHYDE DIMETHYLHYDRAZONE?
6 PhCH2MgCl + CH3CN
7 PhCH2MgCl + CH3CN CeCl3
8 URETHANE + NBS, + PhB(OH)2, Pd
9 15:1 EXTRACT FROM "HYDROSOL" OF SKULL CAP
10 MONOACETYLATION OF SEROTONIN A
11 DIACETYLATIOIN OF SEROTONIN "B"
12 NEUTRAL RESIDUE OF CID-BASE OF SALT ML'S PAGE 172B
13 SHIFF'S BASE, LDA, I(CH2)4I
14 ACETATE (BIS?), NBS
15 URETHANE/IODO, NBS
16 METHYLATE TOSYLATE
17 METHYLATE TOSYLATE, SIM
18 ANATABINE HFB-PROLYL DERIVATIVE
19 ANABASINE HFB-PROLYL DERIVATIVE
20 L ANABASINE (GORROD, PICRATE) HFB PROLYL DERIVATIVE
21 MIX OF ANAB AND ANAT HFB-PROLYL DERIVS, SIM 453 AND 455
22 MA-D2 RXN
23 MA-D2 HFB-PROLYL DERIV
24 RAC MA HFB PROLYL DERIV
25 DMHH-2 172D PURGED OF DMPEA
26 DMHH-4 176A KR'ED SAMPLE
27 DMHH-4 176X HIGH-BOILING DROPLET
28 DMMH 2 169C SUBLIMATE
29 DMMH-2 169D EX HEXANE
30 METHOXY-HYDROXY-HM-4 177B
31 METHYLATION TRY OF 177A 178A
32 XTALS FROM POT OF #31   173-POT
33 TOBACCO EXTRACT, HFB PROLYL DERIVATIVE
34 URETHANE, CARBAMATE, EPL
35 PHENYLACETALDEHYDE O METHYLOXIME
36 MDMH-4 P-146
37 Pr URETHANE, PhB(OH)2, Pd
38 Br URETHANE, PyBEt2, Pd
39 TCH ACETATE, NBS
40 MDMH-4 DILUTED
41 DUBOISIA HOPWOODII, PITURI CPI, HFB-PROLYL
42 N. GLAUCA, HFB-PROLYL
43 RUSSIAN ANABASINE TABLET, HFB PROLYL
44 NEW AMINO ALCOHOL - NaBD4/EF?
45 NORNICOTINE HFB-PROLYL DERIVATIVE
46 MENTHO D0
47 MENTHOL-D4
48 MENTHONE-D0
49 MENTHONE-D2
50 PHENYLACETALDEHYDE DIMETHYLHYDRAZONE

51 PhCH2MgCl + CH3CN
52 PhCH2MgCl + CH3CN CeCl3
53 URETHANE + NBS, + PhB(OH)2, Pd
54 15:1 CONC EXTRACT OF HYDROSOL OF SKULL CAP
55 MONOACETYLATION OF SEROTONIN A
56 DIACETYLATION OF SEROTONIN B
57 PhCH2MgBr + CH3CN, CeCl3, 24 HR
58 PhCH2CHO + H2NN(Me)2
59 MeLi + CeCl3 + DIMETHYLHYDRAZONE
60 MeLi + CeCl3 + DIMETHYLHYDRAZONE, CH3I, 7 DAYS

61 PIPERONAL NS WITH NITROMETHANE P 186
62 AL(HG) ACETIC ACID REDUCTION NEUTRALS P 187
63 AL(HG) ACETIC ACID REDUCTION BASE FRACTION P 187
64 63 DILUTED 10X
65 MONOACETYLATED SEROTONIN TREATED WITH CONC AMMONIA
66 TOH ACETATE, NBS, PhB(OH)2, Pd
67 TOH ACETATE, NBS
68 TOH ACETATE
69 Zn/HCl REDUCTION
done 70 HOMOPIPERONYL NS EX ACOH – page 189
71 HOMOPIPERONYL NS RECOBERED
72 HOMOPIPERONYL FORMAMIDE
73 HOMOPIPERONYLAMINE
74 PyBEt2 + Br-URETHANE (Pd)
75 Ph-TOH

76 75 DILUTED TEN FOLD
77 BENZYL BORANE CH3CN
78 MeCeCl2 + HYDRAZONE, 3 DAYS
79 MeCeCl2 + HYDRAZONE, 3 DAYS, NaBH4/HCHO
80 URETHANE/NBS/NaBH4/Pd
81 URETHANE/NBS/PyBEt2/Pd
done 82 N,N-DIMETHYL-MDPEA PAGE 195 page 195
done 83 MDHH-2 BASE PAGE 194 page 194
done 84 MDHH 4 BASE PAGE 197 page 197
done 85 MDHM 4 BASE PAGE 198 page 198
86 NEUTRALS FROM FORMAMIDE AND POCL3 PAGE 194A
87 Ph-TOH, ACETYLATE
done 88 9.1 MG MS IS (NEUTRAL)
done 89 9.1 MG BASIC EXTRACT

90 MeCeCl2 + HYDRAZONE, EXCESS CeCl3, ADDITIONAL CH3Li

91 MeCl3 RXN. HCl/RT
92 MeCe/HYDRAZONE.HCl. EXTR. HCHO/NaBH4
93 SOLIDS KR MeCeCl2 RXN
94 LIQ KR MeCeCl2 RXN
95 HYDRAZINE/Zn/HOAc EtOH
96 MDA-NS -- TO VERIFY THE ETNO2 IN THE MENO2
97 NEUTRALS, P-199 EXTRACT AND BASE AND KR A,A'DOC
98 DMHM-4 REDUCTION OF QUAT -- P-201
99 NITRONE REACTION, INITIAL
100 NITRONE REACTION, OVERNIGHT

SAMPLE TABLE SM 19 Rev. 3.2 12-May-88

Sample table file name: [redacted] 7 Aug 98 6:51 pm

5

Index Sample Identification
1 YELLOW SAMPLE, BASE FRACTION
2 YELLOW SAMPLE, BASE FRACTION, ACETIC ANHYDRIDE PYRIDINE
3 RED SAMPLE #2, PH09 FRACTION IN TOLUENE
4 RED SAMPLE #3, PH09 FRACTION IN 90/10
5 REFERENCE HALOSTACHINE
6 RED SAMPLE #3, PH09 FRACTION ACETIC ANHYDRIDE
7 REFERENCE HALOSTACHINE, ACETIC ANHYDRIDE
8 143 "ISOLATE FROM C. GIGANTIA
9 145 "ISOLATE" FROM L. GRANDIFLORUS
10 IPHIGENIA ONE BLOSSOM EXTRACTED 90/10
11 IPHIGENIA ONE HALF LEAF, GROUND UP, SPUN, EXTX WITH 90/10
12 NEUTRALS FROM DIMETHYLMETHOXYPEA
13 BASE FROM DIMETHYLMETHOXYPEA
14 DIMETHYLMETHOXYPEA RUN CHCL3 AND NAOH
15 DIMETHYLMETHOXYPEA FROM CLOROX AND HEAT
16 Name Info: DIMETHYLMETHOXYPEA AND CHCL3 AND BASE, RT A FEW MINUTES
17 Name Info: 4-METHOXYPHENETHYLAMINE REFERENCE
18 Name Info: 4-METHOXYPHENETHYLAMINE AND CH2O AND NABH4 AND HOAC IN H2O
19 Name Info: REAL RUN OF 18
20 Name Info: EXTRACT PACH 25% BASE DICHLOR
21 Name Info: 20 ACID BASE -- ENTIRE SAMPLE
22 Name Info: 146A MD-MH
23 Name Info: 10,000 CONC RAZA D'ORO
24 Name Info: CONCENTRATE OF SK
25 Name Info: D2-NICOTINE FROM TARTRATE -- FOR CLINICAL TRIALS
26 Name Info: D4-COTININE DISTILLED BASE -- FOR CLINICAL TRIALS
27 Name Info: (ATS ?)
28 Name Info: D4-COTININE, REMAKING OF THE PERCHLORATE -- BEFORE REXTAL
29 Name Info: D4-COTININE, REMAD PERCHLORATE SALT -- AFTER REXTAL
30 Name Info: D4-COTININE, SAMPLE 29, MUCH DILUTED
31 Name Info: D4-COTININE XTALS FROM ACETONITRILE
32 Name Info: D4-COTININE XTALS #31 DILUTED 10X
33 Name Info: D4-COTININE XTALS #32 DILUTED 10X
34 Name Info: 90/10 BLANK
35 Name Info: 5-HT AND ACETIC ANHYDRIDE
37 Name Info: 35 WASHED WITH AQ. BICARB.
38 Name Info: 90/10 BLANK FOR 3/2/98
39 Name Info: P. HARMALA SAMPLE B EXTRACT
40 Name Info: #39 SAMPLE B DILUTED SEVERAL TIMES
41 Name Info: P. HARMALA SAMPLE A EXTRACT
42 Name Info: #41 SAMPLE A DILUTED SEVERAL TIMES
43 Name Info: XENHET FROM BARK OF VIROLA THEIODORA
44 Name Info: 90/10 EXTRACT OF SERUM TUBE #1
45 Name Info: 43 AGAIN -- METHANOL AND BASE
46 Name Info: 44 DILUTED MUCHO
47 Name Info: 90/10 EXTRACT OF SERUM TUBE 2
48 Name Info: D-0-MECAMYLAMINE
49 Name Info: D-3-MECAMYLAMINE
50 Name Info: O-ETHYL-5-HT

51 Name Info: O-ETHYL-5-HT DMF .5 HR
52 Name Info: O-ETHYL-5-HT DMF 3 HR ACID BASE
53 Name Info: O-ETHYL-5-HT MEONA P 157
54 Name Info: 5-ETO-DET FROM P 157 AFTER ACETIC ANHYDRIDE
55 Name Info: NEUTRALS FROM P 157 AFTER ACETIC ANHYDRIDE
56 Name Info: STEAM DISTILLATE OF T.GRANDIFLORUS
57 Name Info: PJ X-87 3,5-DIBROMOTRIDEUTEROPYRIDINE (LOOK FOR Br,Cl)
58 Name Info: PJ XII-83 3,5-DIBROMOTRIDEUTEROPYRIDINE DIRTY (L.F.Br,Cl)
59 Name Info: 57 A LOT MORE DILUTE
60 Name Info: 0.43 G (0.34 G?) SAMPLE FROM KR

61 HAINES CITRATE AS IS
62 HAINES CITRATE -- BICARBONATE
63 H2 BASE
64 H2 BASE AND BH4
65 HARMINE TCI LOT AJ01
66 HARMINE P-133B
67 HARMINE REGIS LOT-239
68 HARMALINE SIGMA LOT 28C-0433
69 HARMALINE ALDRICH LOT 01021AK
70 HARMALINE ALDRICH LOT 11226PX
71 HARMALINE SIGMA LOT 123H3717
72 [illegible]

SAMPLE TABLE SM18 Rev. 3.2 12-May-88

Sample table file name: [redacted] 13 Oct 97 7:46 pm

Index Sample Identification
1 METHYLATION OF NORNIC D2
2 DIDEHYDROSALSOLIDINE
3 SALSOLIDINE DISTILLED
4 2-METHYLSALSOLIDINE CRUDE
5 PyCHCCOOH/Me3SOH 1 MG/ 4 MG
6 PyCHO/Me3SI/NaH, 24h
7 3-CYANOPYRIDINE
8 NICOTINAMIDE, SYNTHETIC
9 NICOTINAMIDE : SOCl2
10 TRIMETHOPHAN + n-HEX-S-Na
11 WINDOW FOR METHYLQUAT 6/30/97
12 IODOETHYL VIA TsCl/Py/NaI
13 TCH
14 HFB-PROLYL-MDMA NEW REAGENT
15 HFB-PROLYL-MDMA OLD REAGENT

16 HFB PROLYL MDMA OLD REAGENT RECONST AFTER EVAP
17 HFB-PROLYL-MDMA OLD REAGENT ABOUT 1 UG/ML
18 HFB-PROLYL-MDMA OLD REAGENT ABOUT 100 NG/ML
19 HFB-PROLYL-MDMA OLD REAGENT ABOUT 10 NG/ML
20 HFB PROLYL MDMA OLD REAGENT ABOUT 100 NG/ML EVAP/RECONST
21 HFB-PROLYL-MDMA OLD REAGENT ABOUT 10 NG/ML EVAP/RECONST
22 HFB-PROLYL-MDMA 1 UG/ML, NaHCO3 BASE ONLY, 2 HR VORTEX RT
23 HFB-PROLYL-MDMA 1 UG/ML, NaHCO3 + Et3N 2 HR VORTEX RT
24 HFB PROLYL MDMA 1 UG/ML, NaHCO3 + PYRIDINE 2 HR VORTEX RT
25 HFB-PROLYL-MDMA 1 UG/ML, NaHCO3 + DMAP 2 HR VORTEX RT
26 HFB-PROLYL-MDMA 1 UG/ML, NaHCO3, 2 HR VORTEX RT
27 HFB-PROLYL-MDMA 1 UG/ML, Et3N 2 HR VORTEX RT
28 HFB PROLYL MDMA 1 UG/ML,PYRIDINE,2 HR VORTEX RT
29 HFB-PROLYL-MDMA 1 UG/ML, DMAP 2 HR VORTEX RT
30 IODO + PYRROLIDINE

31 SKULL CAP NEUTRAL 90/10
32 MIPT DR
33 PRYIDINEAETIC ACID BUTYL ESTER
34 SKULL CAP PLANT DICHLOR 90/10
35 IODOETHYL, BROMO
36 PYRIDINEACETIC ACID METHYL ESTER
37 PYRIDINE ACETAMIDE (MAYBE)
38 BASIC ALKALOID FRACTION MATUCANA MADISONII
39 BASIC ALKALOID FRACTION TRYCHOCEREUS GRANDIFLORUS
40 BASIC ALKALOID FRACTION NICOTIANA GLAUCA ex ROB N.
41 NICOTINE
42 Py-CHO/Me3SI/BuLi
43 POSSIBLE SALSOLIDINE (SYNTHETIC)
44 METHYLATED T FOR RETENTION TIMES
45 137B REPEAT

46 REFERENCE GRAMINE FOR TIME
47 2-Br-IODOETHYL KR
48 2-I-IODOETHYL
49 PyCHO/Me3SI/NaH
50 PyCHCCOOH/Me3SOH 1 MG/ 4 MG

SM18 continued

51 PyCHO/Me3Si/NaH, 24h
52 3-CYANOPYRIDINE
53 NICOTINAMIDE, SYNTHETIC
54 NICOTINAMIDE : SOCl2
55 NICOTINAMIDE + SOCl2   SIM
56 METHANOL
57 METABOLIC NICOTINAMIDE FROM KCL
58 METABOLIC NORCOTININE FROM NORNICOTINE D6
59 NORCOTININE STANDARD
60 NORNICOTINE-D6 SUBSTRATE FROM TLC, KCL

61 METABOLIC NICOTINAMIDE FROM KCL
62 NICOTINAMIDE STANDARD
63 DIDEHYDROSALSOLIDINE
64 SALSOLIDINE
65 BASIC EXTRACT OF P.p.
66 METHYL NICOTINATE
67 ON COLUMN METHYLATION OF N.A.
68 SALSOLIDINE VIA ACETIC ACID AND NABH4
69 IODOETHYL/Py.HBr.Br2
70 AMINE-ArS?
71 NORNICOTINE-D6
72 PY-EPOXIDE/GLYCOL VIA NaH RXN
73 PY EPOXIDE/GLYCOL VIA NaH RXN SIM 183,166,139,122,100
74 PY-EPOXIDE/GLYCOL VIA NaH RXN ACETATE?
75 NORNIC-D2 SYNTH

76 METHYLATION OF NORNIC D2
77 DIDEHYDROSALSOLIDINE
78 SALSOLIDINE DISTILLED
79 N-METHYLSALSOLIDINE CRUDE
80 NEUTRALS ArS AMINE
81 KR BASE   ArS-AMINE
82 TIMING -- P.p.
83 TIMING -- N-METHYLSALSOLIDINE
done 84 MD ONE #145A —— Page 145 A
85 MD-ENE #145B
86 MD-ANE #146A
87 ZWITTERION FRACTION 137C UNDERIVATIZED
88 Z FRACTION 137C WITH ACETIC ANHYDRIDE/PYRIDINE
89 SOLIDS FROM ACETIC ANHYDRIDE/PYRIDINE
90 ArS tert-AMINE

91 TRIMETHOPHAN : NaBH4
92 WINDOW FOR QUAT RUN
93 ArS-NO2
94 ArSO-NO2 ?
95 Ar SO2 NO2 ?
96 #143 6,7-DIMETHOXY-1,2-DIMETHYL-THIQ
97 CRUDE HORDININE
98 96 #143 DILUTED 10X
99 1 MG EACH NICOTINIC AND PYRIDINE ACETIC ACIDS, 50:50
100

	6,7-Dimethoxy HH	HM	MH	MM	6,7-Methylenedioxy HH	HM	MH	MM
-ine	chem 171, 199, 172	chem 200	chem 140, 169	chem 204	chem 194	chem 196	chem 144, 145, 216	chem
	MS 178, 173	MS	MS 142 (?), 144 (?)	MS	MS 194, 196, 197B	MS ~~196~~ ?	MS 150	MS
	ATLAS (7) (23)		ATLAS (1)		ATLAS (12)		ATLAS (6)	
-one	chem 207, 176	chem 177, 201	chem 206	chem 143, 205	chem 197	chem 198	chem 146	chem
	MS 178	MS 181, 201	MS 142, 162	MS 162, 204	MS ?	MS 198 ~~[illegible]~~	MS 151	MS
		~~[illegible]~~ 7,8-ATLAS 27	conflict					
	ATLAS (24)	ATLAS (4)	ATLAS (2) (17)	ATLAS (3)	ATLAS (13)	ATLAS (14)	ATLAS (9)	ATLAS (25)
AR	ATLAS (19) (HO) 173 178				194 ATLAS (11)		ATLAS (8) (20)	

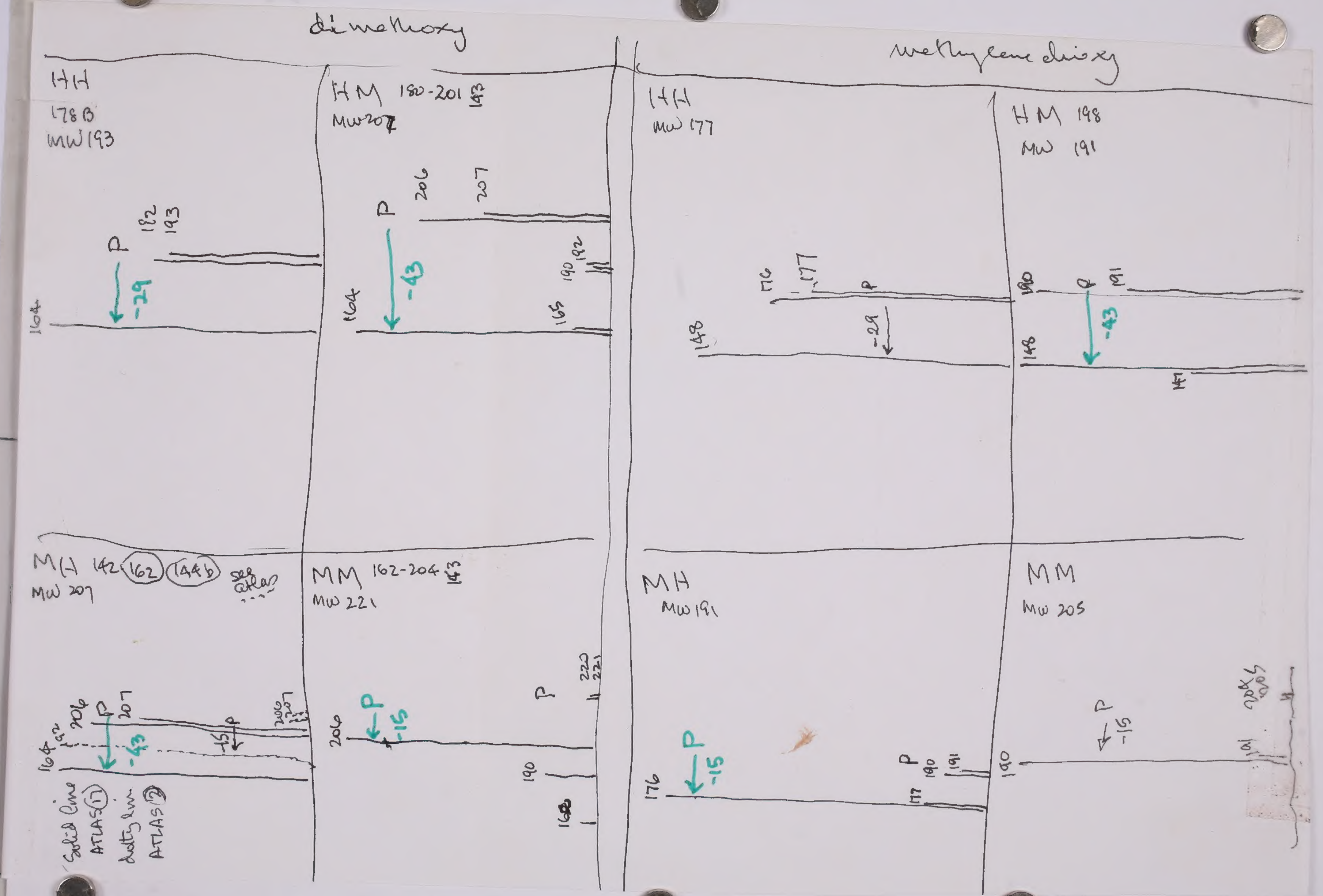
Qhihkal Final Recipes: - in red - typed up! in ☆ Green - NOVA & NMR samples · Hte

6,7 MeO 1 Me	6,7-MeO 1-H	6,7 MDO 1 Me	6,7 MDO 1 H
DMPEA Acetamide (168) (141) (138)	formamide (170) (199)	MDPEA - acetate (209) (145) (215)	229 MDPEA NS (184) (186) 208
DMMH-2 (140)	DMHH - 2 (172) +173, 174, 175! 199,		MDPEA (187) (190) PJ 7-71
DMMM-2⁺ I⁻ (204)			DM-MDPEA (195) 208
DMMM-4 (205) ☆ (143)			MDEDMPEA
DMMH-2 (169)	DMHH-4 (176)	MDMH-2 (145) (216)	MDPEA formamide ~~(171)~~ 191 220
DMMH-4 (206)	DMHM-2 (200)	MDMH-4 (146) (219)	6,7 MDHH-2 (194)
dl-active Salsolidine (225)	DMHM-4 (201) 171 143	MDMM-2 (217)	MDHH-4 (197) 222
			MDHM-2 (196)
			MDHM-4 (198) 23

S (15)
S (16)

ATLAS (25) | ATLAS (9) ATLAS (6) (26) | ATLAS (14) | ATLAS (13) | ATLAS (3) | complete ATLAS (2) (17) | 7-8 ATLAS 27 ATLAS (4) | ATLAS (24)

	6,7-Dimethoxy				6,7-Methylenedioxy			
	HH	HM	MH	MM	HH	HM	MH	MM
1-one: chem	171 199 172	200	140 169	204	194	196	144 145 216	
1-one: MS	178 173		142 (?) 144(?)		194 196 197B	?	150	
	ATLAS (3) (23)		ATLAS (1)		ATLAS (12)		ATLAS (6)	
1-ane: chem	207 176	177 201	206	143 205	197	198	146	
1-ane: MS	178	181 201	142 162	162 204	?	198	151	
		7,8-ATLAS 27	conflict					
	ATLAS (24)	ATLAS (4)	ATLAS (2) (17)	ATLAS (3)	ATLAS (13)	ATLAS (14)	ATLAS (9)	ATLAS (25)
AR	ATLAS (19) CHOT 173 178				194 ATLAS (11)		ATLAS (8) (20) 150 151	



dimethoxy
methylene dioxy
HH
178B
MW 193
P
192
193
164
-29
HM 180-201 143
MW 207
P
206
207
-43
164
190
192
165
HH
MW 177
176
177
P
148
-29
HM 198
MW 191
190
P
191
148
-43
MH 142 162 144b see atlas
MW 207
206
P
207
164
-43
15
P
206
207
solid line ATLAS (1)
dotty line ATLAS (2)
MM 162-204 143
MW 221
P
206
-15
P
220
221
190
MH
MW 191
P
-15
176
P
190
191
177
MM
MW 205
P
-15
190
191